DESCRIPTION

METHOD FOR MANUFACTURING ACTIVATED CARBON, POLARIZABLE

ELECTRODE, AND ELECTRIC DOUBLE-LAYER CAPACITOR

5   TECHNICAL FIELD

The present invention relates to a method for
manufacturing activated carbon, a polarizable electrode,
and an electric double-layer capacitor, and more
particularly to a method for manufacturing activated
10 carbon whereby a carbonaceous material is subjected to
alkali treatment and activated while maintaining a solid
state.

BACKGROUND ART

15   Activated carbon having an excellent adsorption
property is widely used in air cleaning, solvent recovery,
flue-gas desulfurization and denitrification, many types
of industrial wastewater treatment, and other
applications, in addition to its use in catalyst and
20   catalyst carrier applications. In recent years, electric
double-layer capacitors are garnering attention as backup
power sources and auxiliary power sources. Development is
being widely conducted with attention given to the
performance of activated carbon as the electrodes of an
25   electric double-layer capacitor. Electric double-layer
capacitors that use activated carbon as polarizable

electrodes have excellent electrostatic capacity, so
demand is growing rapidly in concert with the development
of the electronics field. In addition to the
miniaturization of conventional power sources for memory
5 backup, and the like, in recent times, development of
large capacity products such as those used in auxiliary
power sources for motors, and the like, is being
conducted.

The principles of electric double-layer capacitors
10 have been long known, but these capacitors have only
started actually being used as devices in recent years.
The electrostatic capacity of electric double-layer
capacitors mainly depends on the surface area of the
polarizable electrodes that form the electric double
15 layer, the resistance of the electrodes, the capacity of
the electric double layer capacitor per unit surface area,
and other factors. In actual application, it is important
to increase the density of the electrodes themselves in
order to increase the electrostatic capacity per unit
20 volume and to decrease the volume of the electric double-
layer capacitor. Conventionally, activated carbon
applications for electric double-layer capacitors have
included (1) activated carbon obtained by activating resin
material, coconut shells, pitch, coal, and the like under
25 acidic conditions using steam, gases or the like (See
"Daiyoryo Kyapashita Gijutsu to Zairyo" (Technology and

Materials for EDLC), CMC Publishing Co., 1998), (2)
activated carbon obtained by a method in which materials
applied in (1) described above have been activated by KOH
and other highly oxidative chemicals (Japanese Patent
5   Application Laid-open No. 10-199767, and other
publications), and the like.

    As described above, high electrostatic capacity and
low resistance are required for electrodes used in
capacitors. However, when activated carbon obtained with
10 the method described in (1) above is used, sufficient
electrostatic capacity cannot be obtained, and a bulky
device is needed in order to obtain the required
electrostatic capacity. According to the method disclosed
in (2) described above, a somewhat high-capacity activated
15 carbon can be obtained by activation with a highly
oxidative activator such as potassium hydroxide. However,
conventional alkali activation is an approach in which an
alkali is heated together with a carbonaceous material to
create a slurry, as disclosed in Japanese Patent
20 Publication No. 62-61529, and handling an alkali in a
dangerous melted state is inevitable. In addition to such
safety problems, conventional alkali-activation technology
for carbonaceous material does not take corrosion of the
device into consideration at all. Therefore, it is
25 difficult to say that this technology can be
advantageously implemented on an industrial basis.

An activated carbon made from a granular isotropic
pitch serving as a raw material is disclosed in Japanese
Patent Application Laid-open No. 2002-104817, which
describes a method for manufacturing activated carbon

5   comprising a wetting step for pitch that wets at least the
surface of a granular mixture of KOH and isotropic pitch
at 200 °C or less, a solidifying step for pitch that
eliminates the wetting step at 400 °C or less to create a
solid state, and a heat treatment step for pitch that

10 performs heat treatment at a temperature greater than
400°C while maintaining the solid state. To reduce the
alkali-induced corrosion of a device, the contact between
the alkali and the device needs merely to be reduced as
much as possible, and from this viewpoint it can be said

15 that treatment in a solid state is a very effective
method. However, according to the disclosure in the
above-stated publication, it is difficult to maintain a
shape and it is apparent that this method still does not
solve the problem of alkali-induced corrosion in a device.

20   An object of the present invention is to provide a
method for manufacturing activated carbon that can reduce
corrosion of a device by alkali, and that has excellent
stability; to provide a polarizable electrode in which
this activated carbon is used; and to provide an electric

25 double-layer capacitor in which this polarizable electrode
is used.

DISCLOSURE OF THE INVENTION

As a result of thoroughgoing research, the inventors perfected the first present invention upon discovering that it is possible to greatly reduce the corrosion of an apparatus during mixing, granulation, dehydration, activation, and other steps by mixing, granulating, dehydrating, and subsequently activating a carbonaceous material and an alkali metal hydroxide while maintaining a solid state.

The second present invention was perfected upon discovering that, upon manufacture activated carbon by subjecting a carbonaceous material to an activation treatment with the aid of an alkali metal activator, not only can the objectives described above be achieved by preparing a mixture of a carbonaceous material and an alkali metal activator, and heat treating, pressure molding, and activating the mixture to manufacture activated carbon, or by preparing a mixture of the carbonaceous material and an alkali metal activator, fabricating a molded form by hot pressing, and thereafter subjecting the system to activation, but it is also possible to manufacture activated carbon with an appropriate specific surface area as an electrode for an electric double-layer capacitor in which the activation efficiency can also be improved by means of an alkali

metal activator, the consumption thereof can be reduced,
and the specific surface area can be controlled, thereby
resulting in higher electrostatic capacity and a small
quantity of impurities.

5   In other words, the first present invention provides
a method for manufacturing activated carbon which
comprises:

a mixing step for mixing a carbonaceous material and
an alkali metal hydroxide while maintaining a solid state;

10   a granulating step for granulating the mixture
obtained in the mixing step while maintaining a solid
state;

a dehydrating step for dehydrating the granules
obtained in the granulating step while maintaining a solid

15 state; and

an activating step for subjecting the dehydration
product obtained in the dehydration step to an activation
treatment to give an activated carbon.

The first present invention also provides a

20 polarizable electrode that is obtained by mixing and
molding the activated carbon obtained in the above manner,
as well as at least a binder and a conductive filler, and
further provides an electric double-layer capacitor in
which this polarizable electrode is incorporated. The

25 first present invention is characterized in that both the
carbonaceous material and the alkali metal hydroxide are

handled in a solid state, and the discovery that corrosion of a device that occurs when manufacturing an alkali-activated carbon can be greatly reduced with excellent safety by means of this manufacturing method is highly

5   innovative.

The present inventors discovered that in the method for manufacturing activated carbon of the first present invention described above, the "alkali metal/carbon" ratio in the surface layer region of the activated carbon raw

10   material dehydration product subjected to the activation treatment is equal to or less than predetermined times of the "alkali metal/carbon" ratio in the center portion, and perfected the invention relating to the activated carbon raw material dehydration product as described below.

15   In other words, the first present invention provides an activated carbon raw material dehydration product obtained by mixing a carbonaceous material and an alkali metal hydroxide while maintaining a solid state, granulating the obtained mixture while maintaining a solid

20   state, and dehydrating the obtained granulated substance while maintaining a solid state; wherein this activated carbon raw material dehydration product satisfies Eq. (1),

$$[M1/C1]/[M2/C2] \leqq 2.4 \qquad\qquad (1)$$

where [M1/C1] is the "alkali metal/carbon" ratio in the

25   surface layer region thereof, and [M2/C2] is the "alkali metal/carbon" ratio in the center portion thereof.

The present inventors also discovered that the
activated carbon obtained by the method for manufacturing
activated carbon of the first present invention described
above exhibits distinctive Raman spectrum characteristics,
5 and perfected the invention related to the activated
carbon as described below.

In other words, the first present invention also
provides an activated carbon obtained by activating a
carbonaceous material with an alkali metal hydroxide,
10 wherein the activated carbon is such that the standard
deviations of the relative peak strengths of the graphite
D band, the amorphous G band, and the graphite G band in
relation to the peak strength of the amorphous D band are
0.05 or less, assuming that the peak strength of the
15 amorphous D band in the Raman spectrum is set to 1 when
20 observation points or more are measured.

The second present invention provides a method for
manufacturing activated carbon by subjecting a
carbonaceous material to an activation treatment with the
20 aid of an alkali metal activator, wherein this
manufacturing method comprises a step for preparing a
mixture of a carbonaceous material and an alkali metal
activator, a step for heat treating the mixture, a step
for using the mixture to obtain a molded product by
25 pressure molding, and a step for using the molded product

to perform the heating process of the activation
treatment.

The second present invention also provides a method
for manufacturing activated carbon by subjecting a
carbonaceous material to an activation treatment with the
aid of an alkali metal activator, wherein this
manufacturing method comprises a step for preparing a
mixture of a carbonaceous material and an alkali metal
activator, a step for using the mixture to obtain a molded
product by hot pressing, and a step for using the molded
product to perform the heating process of the activation
treatment.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional schematic view showing an
example of an electric double-layer capacitor.

BEST MODE FOR CARRYING OUT THE INVENTION

The first present invention is described below.

The method for manufacturing the activated carbon of
the first present invention has the following steps:

a mixing step for mixing a carbonaceous material and
an alkali metal hydroxide while maintaining a solid state;

a granulating step for granulating the mixture
obtained in the mixing step while maintaining its solid
state;

a dehydrating step for dehydrating the granules
obtained in the granulating step while maintaining its
solid state; and

an activating step for subjecting the dehydration
5   product obtained in the dehydration step to an activation
treatment to give an activated carbon.

The principal feature of the manufacturing method of
the first present invention is the working of all of the
steps including the mixing step, granulating step,
10 dehydrating step, and activating step while maintaining a
solid state. One method of maintaining the solid state in
each of these steps is to conduct the treatments at
relatively low temperatures in comparison with
conventional manufacturing methods. The mixture of both
15 the carbonaceous material and alkali metal hydroxide can
be subjected to the activation treatment while maintaining
a solid state with the aid of these low temperature
treatments, in other words, without the conventionally-
required handling of melted alkali metal hydroxide,
20 resulting in a manufacturing method for activated carbon
that reduces the corrosion of the equipment used in these
steps, especially the equipment used during activation,
and that is significantly superior from the point of
safety as well. As long as the solid state is maintained,
25 the solid state referred to in the present invention may

be a wetted state to such an extent that the surface of
the mixture does not adhere.

The raw materials that are used in the mixing step in
the first present invention are described below.

5   The carbonaceous material used in the first present
invention is not particularly limited as long as the
material forms activated carbon by means of activation,
and may be widely selected from plants, minerals, natural
substances, synthetic substances, and the like. Examples
10 of plant-derived carbonaceous material more specifically
include wood, charcoal, coconut shells, and other fruit
shells. Examples of mineral-derived carbonaceous material
include petroleum and/or coal pitch, petroleum coke, coal
coke, pitch, coal, and coke. Examples of natural
15 substances include cotton, hemp, and other natural fibers;
rayon, viscose rayon, and other regenerated fibers; and
acetate, triacetate, and other semisynthetic fibers.
Examples of synthetic materials include nylon, and other
polyamides; vinylon, and other polyvinyl alcohols;
20 polyethylene, polypropylene and other polyolefins; and
polyurethane, phenolic resin, and the like.

Examples of preferred carbonaceous materials that may
be used as starting materials for an activated carbon
include easily graphitizable carbonaceous material, for
25 example, petroleum coke, coal coke, pitch, coal, coke,

petroleum pitch, mesophase pitch, polyvinyl chloride, polyimide, polyacrylonitrile.

Among these, mesophase pitch is preferable, and carbon fiber based on mesophase pitch is more preferable as the carbonaceous material. A pitch containing 50 vol% or more, or preferably 80 vol% or more, of an optically anisotropic phase is desirable from the viewpoint of high conductivity.

The shape of the carbonaceous material is not particularly limited. A granular form, powder form, fiber form, sheet form, or other form may be used.

Examples of carbonaceous materials in a fiber or sheet form include woven or nonwoven fabric, film, felt, or other materials in the form of a sheet composed of cotton or other natural cellulose fiber; viscose rayon, polynosic rayon, or other regenerated cellulose fiber; isotropic pitch fiber, mesophase pitch fiber, or other pitch fiber; or pulp fiber, polyvinyl alcohol fiber, ethylene vinyl alcohol fiber, phenol fiber, or other synthetic fiber.

In the first present invention, a carbonaceous material that is milled is preferably used, but one having a maximum length of 500 μm or less in the direction of the major axis is preferably used, and one that is 200 μm or less is more preferably used to effectively advance the activation treatment described below. The maximum length

in the direction of the major axis may be confirmed by
observing an electron microscope photograph of the
pulverized powder of carbonaceous material extracted at
random, for example. Pulverization may be performed by
5   means of well-known pulverizers such as cone crushers,
double roll crushers, disk crushers, rotary crushers, ball
mills, centrifugal roll mills, ring rolling mills, and
centrifugal ball mills.

Examples of the alkali metal hydroxide used in the
10 first present invention include, for example, granular
forms of sodium hydroxide, potassium hydroxide, lithium
hydroxide, and cesium hydroxide, or mixtures of these.
Sodium hydroxide and/or potassium hydroxide are preferably
used to obtain a carbonaceous material having large
15 electrostatic capacity. Common commercially available
products may be used as these alkali metal hydroxides.

From the viewpoint of the moisture content, it is
preferable for the moisture content of such an alkali
metal hydroxide to be 1 to 20 wt%, and a content of 1 to
20 10 wt% is even more preferred in view of handling.

In the first present invention, it is preferable to
use a pulverized alkali metal hydroxide, and from the
viewpoint of the average size of the particles, such an
alkali metal hydroxide preferably has an average particle
25 diameter of 1 mm or less. The same pulverizers used to
pulverize the carbonaceous material may also be used to

pulverize the alkali metal hydroxide. In the particular case that the alkali metal hydroxide takes the form of a bulk, such as a block, the block need merely be pulverized with a pulverizer such as those described above to form

5   granules. Here, granules broadly refer to common fine granular states such as spherical shapes, fractured shapes, and powder shapes.

Each step of the method of manufacturing the activated carbon of the first present invention is

10   subsequently described.

(Mixing step)

First, the carbonaceous material and the alkali metal hydroxide are mixed while maintaining a solid state. At this time, the system should be sufficiently mixed so as

15   to achieve as much uniformity as possible. It should also be noted here that a solid state refers to the mixture in a solid state. The mixer used in this step is not particularly limited, but well-known rotary container-type mixers, fixed container-type mixers, or the like may be

20   used. A rotary container-type mixer is preferred in that a uniform mixing can be achieved.

An alkali metal hydroxide is normally hygroscopic, so the components are preferably mixed under a dry air, dry nitrogen, or other dry environment to avoid moisture

25   absorption. Nickel is preferably used as the mixer material to reduce corrosion as much as possible.

The mixing temperature is not particularly limited, but mixing at room temperature is normally sufficient. If the quantity of alkali metal hydroxide is too small, then the properties of the objective carbon material become
5   variable because the activation treatment is insufficient and nonuniform, and if the quantity is conversely too large, not only is the treatment uneconomical, but activation also advances too far. As a result, while the electrostatic capacity of carbonaceous material per unit
10 weight tends to become higher, the electrostatic capacity of the carbonaceous material per unit volume may decrease. The quantity of alkali metal hydroxide may therefore be one or more parts by weight per one part of the carbonaceous material, preferably 1.2 to 4 parts by
15 weight, more preferably 1.3 to 3 parts by weight per one part by weight of the carbonaceous material.

When mixing the carbonaceous material and the alkali metal hydroxide in this mixing step, the carbonaceous material is preferably added to the alkali metal hydroxide
20 in advance and finely pulverized, and the carbonaceous material and the alkali metal hydroxide are mixed thereafter. In this case, if the quantity of the carbonaceous material added to the alkali metal hydroxide in advance is too small, then insufficient effect is
25 manifested, and if the quantity is too large, then the ability of the system to be pulverized is lowered, so

preferably 0.5 to 10 wt% of carbonaceous material may be added to the alkali metal hydroxide, and more preferably 1 to 5 wt% may be added. By mixing and pulverizing in this manner, a bridge cannot be formed between the alkali metal

5   hydroxide particles, so the mixing of carbonaceous material and alkali metal hydroxide can be improved and a uniform mixture can be obtained, with little variation in the composition ratio of the alkali metal hydroxide and the carbonaceous material in the granulation and/or

10   dehydration product, which is prepared in the granulating and/or dehydrating steps described hereinafter. An activated carbon with excellent electrostatic capacity, little activation nonuniformity, and no variability in performance can be obtained from such a mixture.

15   The alkali metal hydroxide to which the carbonaceous material has been added in advance is finely pulverized in accordance with a batch or continuous process using a ball mill, a dynamic mill, or other well-known pulverizing apparatus. An alkali metal hydroxide is commonly

20   hydroscopic and deliquescent, so pulverizing may preferably be performed under an environment of nitrogen, helium, argon, or another inert gas that does not contain moisture or low dew-point air at about −10 °C or less. The pulverizing conditions depend on the kind of alkali

25   metal hydroxide, the flake particle size, the kind of carbonaceous material, the shape, the pulverizing

apparatus, and other factors, so one unique set of
conditions cannot be determined, but when the alkali metal
hydroxide is potassium hydroxide flakes, and the
carbonaceous material is a mesophase pitch carbon fiber (a
5   cylindrical shape with a diameter of 13 μm and a length of
20 μm), for example, a uniform pulverized product with
excellent fluidity and an average particle diameter of
about 10 μm can be obtained without bridge formation when
a ball mill composed of nylon resin and filled with an
10   aluminum ball is operated for one to two hours at a
circumferential speed of about 1 m/sec.

(Granulating step)

Next, the mixture obtained in the mixing step is
preferably granulated in spherical shapes while
15   maintaining the solid state thereof. Here, because the
granulation effect is not manifested when the temperature
of the granulation treatment is too low, the temperature
may preferably be 80 °C or higher while maintaining the
required solid state as the granulation treatment
20   condition. The pressure of the granulation treatment at
this time is not particularly limited. More preferable
conditions for the granulation treatment are a reduced
pressure of 0.01 to 300 Torr for the granulation treatment
pressure, and 90 to 140 °C for the granulation treatment
25   temperature. The temperature rise rate until achieving
such a granulation treatment temperature is not

particularly limited, but may be conducted at a rate of about 0.1 to 10 °C/minute.

The granulation treatment may be conducted under an environment of inert gas such as nitrogen.   The granulation may be performed with the mixers described above, but if the granulation product is too large, then dehydration nonuniformity occur, activation does not reach sufficiently deep into the mixture, and activation defects may occur, so the maximum diameter is preferably 50 mm or less.   Conversely, if the granulation product is too small, then powdering occurs and the product easily adheres to the wall of the container and becomes difficult to remove from the container, so the maximum diameter is more preferably 1 mm to 30 mm.   The granules of the granulation product may be adjusted by the rotation of the mixer used.

(Dehydration step)

The granulation product obtained in the granulation step is subjected to a dehydration treatment while maintaining the solid state thereof to obtain a granulated dehydration product (in other words, a dehydrated granulation product).   The dehydration treatment may be performed with the same mixers described above, but a separate reactor may also be used.   Here, assuming that a solid state is maintained, the temperature of the dehydration treatment is preferably kept at 200 °C or

higher as a condition for the dehydration treatment because dehydration tends to be insufficient if the dehydration temperature is too low, and activation occurs before sufficient dehydration is performed if the temperature is too high. More preferable conditions for the dehydration treatment are a reduced pressure of 0.01 to 10 Torr for the dehydration treatment pressure, and 200 °C to 400 °C for the dehydration treatment temperature.

The temperature rise rate is preferably adjusted to maintain the solid state. The temperature rise rate depends on the amount of reduced pressure, but a rate of about 0.1 to 10 °C/minute is preferable, and 0.2 to 5 °C/minute is more preferable. The dehydration treatment may be conducted under a flow of inert gas such as nitrogen.

Here, the dehydration treatment is preferably conducted so as to satisfy Eq. (2) below, which defines the correlation between the temperature rise rate and the pressure inside the treatment system at which dehydration can be performed while maintaining the solid state during the dehydration treatment in the first present invention.

$$P v < 15 \qquad\qquad (2)$$

In the equation, P is the pressure (Torr) during the dehydration treatment, and v is the temperature rise rate (°C/minute) during the dehydration treatment. The reason

why the dehydration treatment is conducted so as to
satisfy Eq. (2) is as below.

Namely, if the temperature of the mixture
(hereinafter simply referred to as "raw material") of the
pulverized carbonaceous material and the granulated alkali
metal hydroxide rises under a small quantity of air or
inert gas flow at normal pressure, the alkali metal
hydroxide in the raw material melts at a temperature that
corresponds to the moisture content of the raw material,
and the raw material forms a slurry or a liquid. For
example, if the temperature is allowed to rise under
atmospheric pressure, the raw material enters a wetted
state at about 250 °C, the particles begin to mutually
adhere, and eventually the system becomes a slurry. Such
a condition must be avoided to the extent possible from
the viewpoint of alkali corrosion of the device. When the
dehydration treatment is conducted so as to satisfy
Eq. (2), water contained in the raw material can be
released as water vapor while maintaining the solid state
of the raw material, the moisture content therein can be
reduced, and, as a result, the dehydration treatment can
be performed while maintaining the solid state.

More specifically, if the temperature is allowed to
rise to 300 °C at a rate of 0.8 °C/minute, for example,
dehydration can be conducted until the moisture content
reaches 0 % while maintaining the solid state if the

pressure inside the system is kept to 10 Torr or less. If
the temperature is allowed to rise to 300 °C at a rate of
2.0 °C/minute, dehydration can be conducted until the
moisture content reaches 0% while maintaining the solid
state if the pressure inside the system is kept to 3 Torr
or less. If the pressure inside the system is 10 Torr
when the temperature rise rate is 2.0 °C/minute, the raw
material enters a slurry state at 250 °C, the particles
begin to mutually adhere, and the solid state may not be
capable of being maintained.

The temperature rise rate in the dehydration
treatment is not limited to a uniform temperature raise,
but the pressure inside the system and the temperature
rise rate may be freely modified as long as the
relationship noted above is satisfied. It is also
possible to reinitiate a temperature rise after holding a
fixed temperature during dehydration, or to reinitiate
dehydration after once the temperature has been lowered.

If the temperature during the dehydration treatment
is too low, then dehydration tends to be insufficient, as
described above, and if too high, then activation occurs
before dehydration is sufficiently completed, and
hydrogen, methane, or other combustible gases are
generated. The temperature is therefore preferably 200 °C
to 400 °C, but when handling combustible gas under reduced
pressure conditions, the temperature during the

dehydration treatment is preferably kept at 350 °C or less under reduced pressure in order to prevent ignition, explosion, or the like due to oxygen leaking from outside the system. If the temperature is allowed to rise greater
5   than this, then switching over to increasing the temperature at normal pressure is preferred from the standpoint of safety. With respect to the end temperature under reduced pressure, if the moisture content reaches 0%, then there is no particular limit, but when using
10   mesophase pitch carbon fiber as the carbonaceous material, then it is preferable to perform operations under reduced pressure up to 300 °C.

     The granulation and dehydration steps are preferably carried out so as to satisfy Eq. (3) below,

15        $[A1/B1] \geqq [A2/B2]$ (3)

where A1 (N) is the crushing strength of the granulation product obtained in the granulation step described above, B1 (cm) is the diameter of the granulation product, A2 (N) is the crushing strength of the dehydration product
20   obtained in the dehydration step, and B2 (cm) is the diameter of the dehydration product. Activation nonuniformity between the particles of activated carbon can thereby be reduced. Specific treatment conditions that satisfy Eq. (3) can be set by appropriately adjusting
25   the granulation treatment and dehydration treatment conditions. Here, the crushing strength (N: newtons) of

the granulation product and/or the dehydration product is the value measured by tightly holding the granulation or dehydration product in the direction of the minor axis with a compression jig, and compressing the system at a compression speed of 10 mm/minute from such a state with the aid of a commercially available dynamic strength measuring apparatus capable of measuring crushing strength (Autograph AG-5000B manufactured by Shimadzu Corp., for example). The diameter of the granulation or dehydration product is the length of the minor axis (cm) when tightly held with the compression jig in the direction of the minor axis of the granulation or dehydration product. It is preferable to use the average value of at least 20 granulation or dehydration products for the numerical value of the [A1/B1] ratio or [A2/B2] ratio.

The dehydration product obtained in the main dehydration step by way of the mixing and granulation steps described above; namely, the dehydration product obtained by mixing the carbonaceous material and the alkali metal hydroxide while maintaining a solid state, granulating the obtained mixture while maintaining the solid state thereof, and dehydrating the obtained granulation product while maintaining the solid state thereof, is useful as an activated carbon raw material. In particular, the dehydration product that satisfies the Eq. (1) below

$$[M1/C1]/[M2/C2] \leqq 2.4 \qquad (1)$$

where $[M1/C1]$ is the alkali metal/carbon ratio in the
surface layer region of the dehydration product, and
$[M2/C2]$ is the alkali metal/carbon ratio in the center

5   portion of the dehydration product, can provide a stable-
quality activated carbon in which activation defects
between particles are small, so the product is very useful
as an activated carbon raw material dehydration product.
The alkali metal/carbon ratio in the surface layer region

10 and the center portion of the dehydration product is a
value obtained by bisecting the dehydration product at
substantially the center portion, finding the
potassium/carbon ratio by performing an X-ray analysis on
both the surface layer region and the center portion with

15 a scanning electron microscope, and dividing the
potassium/carbon ratio $[M1/C1]$ in the surface layer region
by the potassium/carbon ratio $[M2/C2]$ in the center
portion. Here, the surface layer region refers to the
portion between 50 μm and 550 μm from the surface of the

20 dehydration product toward the center portion thereof, and
the center portion refers to the portion of within 500 μm
or less from the center of the molded product. It is
preferable to use the average value of at least
20 granulation or dehydration products for the numerical

25 value of the alkali metal/carbon ratio.

    (Activation step)

Activated carbon is subsequently obtained by
subjecting the dehydration product obtained in the
dehydration step to an activation treatment. Here, the
activation treatment can be performed continuously or in a
5   batch in an inert gas such as nitrogen or argon. If the
temperature of the activation treatment is too high, the
surface area of the activated carbon is increased, but the
electrostatic capacity is reduced when fashioned into an
electric double-layer capacitor, and because the metallic
10   potassium vaporized by the activation treatment
evaporates, the danger is significantly increased. If the
temperature of the activation treatment is too low, the
fine structure that is to be gasified and removed from the
system by the activation treatment is not removed, so the
15   electric resistance increases when the product is used as
an electrode material, for example. The temperature of
the activation treatment is therefore preferably 500 °C to
900 °C, and more preferably 550 °C to 800 °C.

When performing the activation treatment, the
20   temperature must rise to a predetermined activation
treatment temperature (holding temperature), but a rapid
temperature rise is not preferred from the point of
maintaining the granular shape of the hydration product,
and a temperature rise that is too slow may result in
25   inadequate performance as an electric double-layer
capacitor, so it is normally preferable to adopt a

temperature rise rate of 50 °C to 1,000 °C/hour. It is
desirable to further dry the granular dehydration product
(in other words, the dehydrated granulation product) by
exposing the system to a flow of inert gas such as
5   nitrogen or argon prior to the activation treatment.

When sodium hydroxide or potassium hydroxide is used
as the alkali metal hydroxide, the activation treatment
temperatures are each in the vicinity of 650 °C or 730 °C,
and the electrostatic capacity of the obtained activated
10   carbon increases critically. The temperature rise rate in
the activation treatment in this case is preferably about
4°C per minute beginning from room temperature.

Specific examples of the temperature rise rate to the
predetermined activation temperature (holding temperature)
15   and the holding time at the predetermined activation
temperature in the activation step include a rate at which
the temperature is allowed to rise to 200 to 600 °C at
preferably 5 °C/minute or less, and more preferably 2
°C/minute or less; an activation treatment temperature
20   (holding temperature) of 700 °C or more, and more
preferably 700 to 850 °C; and a holding time of preferably
0.5 to 8 hours, and more preferably 1 to 6 hours.

A conventional rotary type, fluid type, moving type,
or other type of activation device may be adopted as the
25   activation device. A material having nickel as a main
component is preferably used as the material of the

activation device from the viewpoint of reducing corrosion
as much as possible. From the viewpoint of industrial
dominance with regard to the activation device and the
treatment method, a rotary kiln from the category
5   described above is preferred as the activation device, and
an externally heated rotary kiln is more preferred; and a
continuous-type treatment method is preferred from the
aspects of productivity and the performance of the
activated carbon.

10   When exposing the inside of the activation device to
a flow of inert gas during the activation treatment, the
inert gas inside the activation device is normally
circulated at a flow rate of 0.01 cm/minute or more, and
0.1 cm/minute or more is preferred, though this varies
15   according to the reaction method used.

The obtained treatment product is cooled after the
activation treatment is complete. Cooling may be
performed under a flow of inert gas such as nitrogen or
argon in order to avoid combustion of the treatment
20   product (activated carbon). The objective activated
carbon may be subsequently obtained by washing the
treatment product with water to remove the alkali metal
portion, and drying the product by an ordinary method.

As described above, the mixture of carbonaceous
25   material and alkali metal hydroxide is entirely treated
while maintaining the solid state. Thus, the mixture is

consistently treated to activation without melting, so
oxidative corrosion can be markedly reduced.

At least the activation step of the manufacturing
method of the first present invention is preferably
conducted under a flow of inert gas, as described above.
This inert gas functions as a carrier of the alkali metal
in the form of vapor generated from the activated
treatment product by heat during the activation treatment,
but the alkali metal in this vapor form is highly reactive
and is greatly susceptible to the danger of ignition or
explosion. As a result, this metal in vapor form is
preferably circulated through the activation system
together with the inert gas as a carrier thereof, and
allowed to adhere to the sorptive carbon material to
deactivate the vapor in the present invention. This
approach resolves the problem of ignition or other
unwanted combustion even if the sorptive carbon material
and the activated carbon material are released to the
atmosphere after sorption. Here, sorption widely refers
to collecting, capturing, or the like, including
adsorption.

During sorption, the inert gas containing alkali
metal in the form of vapor is preferably brought into
contact with the sorptive carbon material for 0.5 seconds
or more, and more preferably 1.0 seconds or more. If the
sorption time is less than 0.5 seconds, the deactivation

of the alkali metal in vapor form through sorption to the
sorptive carbon material is insufficient, and the alkali
metal tends to pass to the exterior of the system as vapor
without being sorbed by the sorptive carbon material.

5   Also during sorption, the temperature of the sorptive
carbon material is preferably set to 300 to 800 °C, and
more preferably to 400 to 700 °C. A temperature less than
300°C results in insufficient deactivation of the alkali
metal by the sorptive carbon material, and a temperature
10   higher than 800 °C results in the sorptive carbon material
itself being activated and deteriorated, so the strength
may consequently be reduced and the product may become
more susceptible to fine powdering or other undesirable
effects.

15   Also during sorption, if the linear velocity of the
inert gas is too high then the alkali metal in vapor form
may blow through without making contact with the surface
of the sorptive carbon material, and if too low the
concentration of the alkali metal in vapor form may rise.
20   As a result, deactivation tends to be insufficient due to
residual alkali metal vapor that is not able to make
contact with the carbon material, or due to deposition or
the like on the sorbed alkali metal, so the linear
velocity of the inert gas is preferably set to between 1.0
25   and 10.0 mm/second.

Examples of carbon materials for sorption that can sorb an alkali metal in vapor form during sorption include activated carbon, carbon fiber mat, silica gel, alumina, ceramic, ceramic wool, and a composite product of

5   activated carbon with ceramic wool, but among these, activated carbon is preferred. A wide range of examples of carbonaceous materials that yield activated carbon by activation with conventional activation methods includes coconut shells, petroleum pitch, coal pitch, phenolic

10   resin, mesophase pitch carbon fiber, and other carbonaceous materials. The shape of the carbonaceous material is not particularly limited. A granular form, powder form, fiber form, sheet form, or other form may be used. It is preferable to use activated carbons that have

15   a large specific surface area, and that contain a greater quantity of aromatic ring edge structures and functional groups for reacting with alkali metal. These activated carbons are normally used independently, but a plurality of types may be mixed and used.

20   The quantity of sorptive carbon material to be used depends on the type and shape of the carbonaceous material, on the activation method, the loading method, treatment temperature, and other factors, but if the amount is too small then the breakthrough point of the

25   alkali metal sorption is exceeded, deactivation due to reaction with the alkali metal does not complete, the

alkali metal is left behind, and ignition or other danger
remains; and if too much is used the process is
uneconomical, so the metal portion in the alkali metal
hydroxide is preferably a weight multiple of 0.1 to 3.0,
5   and more preferably a weight multiple of 0.2 to 2.0.

      Once the heat treatment as an activation treatment is
completed, the sorptive carbon material to which alkali
metal has been sorbed may be reused as sorptive carbon
material by washing and drying. When the sorptive carbon
10 material and the carbonaceous material, which is the raw
material for manufacturing the objective activated carbon
material, are the same, the sorptive carbon material that
was used to sorb alkali metal may also serve as the raw
material for obtaining the objective activated carbon
15 material. The alkali metal sorbed to the sorptive carbon
material is eluted as alkali metal hydroxide in an aqueous
phase when the sorptive carbon material is washed with
water, so the alkali metal can be recovered as alkali
metal hydroxide from the aqueous solution thereof.
20 Activation nonuniformity stemming from a nonuniform
mixture condition and heat history observed when the
mixture of carbonaceous material and alkali metal
hydroxide is directly carried into the activation
treatment can be prevented, and deactivation with the
25 carbon material of the generated alkali metal in vapor
form can be conducted under stable conditions. An

industrially advantageous manufacturing method for
activated carbon can therefore be obtained by allowing the
metal in vapor form and the inert gas that functions as a
carrier thereof to flow through the activation system,
5   sorbed to the sorptive carbon material, and deactivated.

As described above, according to the manufacturing
method of the first present invention, not only can
industrially advantageous alkali activation be performed
because corrosion of the device itself is minimal, but the
10   metal portion contained in the activated carbon can also
be markedly reduced, preferably to 300 ppm or less.   In
particular, the iron, copper, and nickel contents can each
be reduced to 20 ppm or less, and more preferably to
10 ppm or less.   An electric double-layer capacitor having
15   excellent self-discharge characteristics can be
manufactured by using polarizable electrodes obtained by
molding this activated carbon.

Distinctive Raman spectrum characteristics are
exhibited when an easily graphitizable carbonaceous
20   material is used as the carbonaceous material.   That is to
say, this activated carbon is such that the standard
deviations of the relative peak strengths of the graphite
D band, the amorphous G band, and the graphite G band in
relation to the peak strength of the amorphous D band are
25   0.05 or less, assuming that the peak strength of the
amorphous D band in the Raman spectrum is set to 1 when

20 observation points or more are measured. An activated
carbon with a structurally stable quality is achieved by
minimizing the standard deviations in such a manner.

5   Here, the peak strength of the amorphous D band, the
peak strength of the graphite D band, the peak strength of
the amorphous G band, and the peak strength of the
graphite G band are the peak strengths in the Raman
spectrum obtained by curve fitting the peak in the
vicinity of 1,250 cm^{-1}, the peak in the vicinity of
10 1,350 cm^{-1}, the peak in the vicinity of 1,550 cm^{-1}, and the
peak in the vicinity of 1,600 cm^{-1}, respectively, with a
Gaussian function and thereby dividing these respectively
into four bands, the peak indicating the amorphous D band,
the peak indicating the graphite D band, the peak
15 indicating the amorphous G band, and the peak indicating
the graphite G band, where the Raman spectrum is measured
using an Nd^{3+}:YAG laser with a wavelength of 532 nm for
the excitation light, and a charge coupled device (CCD)
for the detector.

20   In such a polarizable electrode, if the electrode
density is too small, then the electrode surface area
becomes larger and the electric double layer capacitor
become too bulky, so the density is preferably 0.80 g/cc
or higher.

25   It is possible to apply conventional methods to
manufacture a polarizable electrode for an electric

double-layer capacitor using the activated carbon obtained
with the manufacturing method of the first present
invention. Materials known as binders, such as
commercially available polyvinylidene fluoride, and
5   polytetrafluoroethylene, for example, may be added and
kneaded as required up to about several percent, and
thereafter placed in a mold, pressure molded, calendered
into a sheet, and punched out into a required shape to
fashion an electrode. In this process, alcohol, N-methyl
10   pyrrolidone, or other organic compounds; water, or other
solvents; dispersants; and various additives may be used
as required. Heat treatment may be performed in the
process. Temperatures higher than that required not only
cause the binder component to deteriorate, but also affect
15   the surface structure properties, such as the specific
surface area, for example, of the activated carbon
component, so it is apparent that the temperature
conditions thereof must be considered.

When molding, conductive substances such carbon
20   black, Ketjen black, or other conductive carbons may be
added to reduce the resistance of the electrode. This is
effective in reducing the internal resistance of the
polarizable electrode, and in making the volume of the
electrode smaller. In addition to a sheet electrode such
25   as that described above, a kneaded product may be applied
to a collector to fashion a coated electrode.

The polarizable electrode described above is useful
as an electrode for an electric double layer capacitor
such as that shown in Fig. 1 (a schematic cross-sectional
view). Other than using the polarizable electrode
5   according to the present invention, the constituent
components comprising the capacitor in Fig. 1 may have the
same configuration as a conventional electric double-layer
capacitor, and in the figure, for example, 1 and 2 are
collector members comprising aluminum or the like; 3 and 4
10   are polarizable electrodes comprising the activated carbon
of the present invention; 5 is a separator comprising a
polypropylene unwoven fabric or the like; 8 is a gasket
comprising polypropylene, polyethylene, polyamide,
polyamide imide, polybutylene, or the like; and 6 and 7
15   are respectively a cover and a case comprising stainless
steel or the like.
     An electrolytic solution 9 in which
tetraethylammonium tetrafluoroborate, tetramethylammonium
tetrafluoroborate, triethylmethylammonium
20   tetrafluoroborate, or another conventional electrolyte is
dissolved in a solvent such as tetrahydrofuran or another
ether; dimethyl carbonate, diethyl carbonate, ethylene
carbonate, propylene carbonate, dimethyl carbonate,
diethyl carbonate, or another carbonate; acetonitrile or
25   another nitrile; γ-butyrolactone, α-methyl-γ-
butyrolactone, or another lactone; dimethylsulfoxide or

another sulfoxide; or dimethylformamide or another amide, must be sealed within the case 7 to allow the system to function as an electric double-layer capacitor.

The electric double-layer capacitor having the configuration shown in Fig. 1 uses the activated carbon of the first present invention, so the electrostatic capacity can be set to 30 F/cc or more. The retention rate of the electrostatic capacity can be maintained at 90% or more even after repeating charging and discharging at least 500 times, the charging and discharging consisting of charging with a constant current and discharging with a constant current.

The second present invention is subsequently described.

The method for manufacturing activated carbon of the second present invention entails manufacturing activated carbon by subjecting a carbonaceous material to an activation treatment with the aid of an alkali metal activator, this manufacturing method having a step for preparing a mixture of a carbonaceous material and an alkali metal activator, a step for heat treating the mixture, a step for using the mixture to obtain a molded product by pressure molding, and a step for using the molded product to perform the heating process of the activation treatment. The method for manufacturing activated carbon of the second present invention

alternatively has a step for preparing a mixture of a carbonaceous material and an alkali metal activator, a step for using the mixture to obtain a molded product by hot pressing, and a step for using the molded product to

5 perform the heating process of the activation treatment. Thus, the second present invention improves the activation efficiency by means of the alkali metal activator, reduces the quantity thereof consumed, makes control of the specific surface area possible, and thereby provides an

10 activated carbon that has a high electrostatic capacity, that is devoid of impurities, and that additionally has a suitable specific surface area as an electrode for an electric double-layer capacitor.

     In the second present invention, a molded product is

15 formed before the activation treatment. In this molded product, the alkali metal-containing activator is in close contact with, and is uniformly dispersed in, the carbonaceous material, and the thermal conductivity is also high, so the efficiency of activation by means of the

20 alkali metal activator can be improved, and the quantity of the activator consumed can be reduced from conventional methods. The shape of the molded product can also be maintained substantially completely or in a slightly broken down state until the completion of the heating

25 process, so it is possible to retain substantially the whole quantity of alkali metal therein.

According to the second present invention, it is therefore possible to obtain activated carbon that is sufficiently activated by a small quantity of alkali metal-containing activator, and that has high

5   electrostatic capacity density and a small quantity of impurities; and also to obtain activated carbon in which the specific surface area can be controlled by means of the amount of alkali metal, and that is provided with a suitable specific surface area as an electrode for an

10 electric double layer capacitor. Furthermore, the elution from the molded product of the alkali metal-containing activator is prevented or decreased, so it is possible to prevent or inhibit the corrosion of the reactor, and to improve the durability thereof.

15   The carbonaceous material described in the first present invention may be used as the carbonaceous material in the second present invention. In addition to the alkali metal hydroxide described in the first present invention, an alkali metal may also be used alone as the

20 alkali metal activator. The method of manufacturing activated carbon of the second present invention is described step-by-step below.

Mixture preparation step

The carbonaceous material and the alkali metal

25 activator both are preferably used in a powder form, but the moisture content of both of these should be kept very

low in order to inhibit melting of the activator. A ball
mill, jet mill, high-speed rotating mill, or the like may
be used as the pulverizer for obtaining powders of these.
The average particle diameter d_1 of the powder of the
5   carbonaceous material is preferably set to 1 μm or more
and 50 μm or less, and the average particle diameter d_2 of
the powder of the alkali metal activator is preferably set
to 5 μm or more and 50 μm or less.

With regard to the blend ratio of the two in terms of
10 weight, the weight ratio $[W_2/W_1]$ is preferably set to 2.5
or less, and more preferably to 2.0 or less, where the
weight of the powder of the carbonaceous material is W_1,
and the weight of the powder of the alkali metal activator
is W_2. This is due to the fact that if the ratio $[W_2/W_1]$
15 thereof exceeds 2.5 then the alkali metal activator melts
more easily, inviting the possibility of reactor
corrosion, impurities becoming mixed into system, and
other unwanted outcomes. If the ratio $[W_2/W_1]$ thereof is,
conversely, less than 0.3 then the specific surface area
20 of the activated carbon tends to fall below 300 m^2/g, and
the electrostatic capacity also tends to decrease. The
ratio $[W_2/W_1]$ is therefore preferably 0.3 or more, and more
preferably 0.5 or more. An even more preferable range for
the ratio $[W_2/W_1]$ is 0.5 or more and 2.0 or less. The
25 electrostatic capacity of the activated carbon is thereby
greatly increased.

A cutting mixer may be used when mixing the powders
of the carbonaceous material and the alkali metal
activator, and the use of this mixer allows both powders
to be uniformly mixed.

5   Heating treatment step

It is preferable to perform the heating treatment on
the powder mixture over a maximum period of 24 hours, with
the heating temperature T set to 300 °C or less during
molding to increase the binding capacity of the alkali

10   metal-containing activator in the molded product. The
alkali metal activator softens and the entire powder
mixture becomes viscous in an intermediate stage of this
heating treatment, and the viscous material is thereafter
converted to a solid by means of evaporation of the

15   moisture content. If the heating temperature T exceeds
300°C then the alkali metal activator completely melts,
inviting the possibility of reactor corrosion, impurities
becoming mixed into system, and other unwanted outcomes.
If the heating temperature T is, conversely, less than 100

20   °C then the entire powder mixture does not become viscous,
and the moisture content does not evaporate, so the
significance of the heating treatment may possibly be
lost. The preferred lower limit of the heating
temperature T is therefore 100 °C.

25   Molding Treatment Step

Pressure molding is performed to improve the deformation strength of the molded form in the heating process under high temperature. After the heating treatment is complete, the pressure P applied to the solid product before cooling or after cooling is preferably set to 2 MPa or more, and more preferably to 10 MPa or more. If the pressure P is less than 2 MPa then the deformation strength of the molded product may be too low. If the pressure P is 40 MPa or more then the molded product becomes highly dense, activation inside the molded product does not adequately progress, and not only does variation in the specific surface area become greater, but the measurement thereof also tends to become more difficult, so the preferred range of pressure P is 2 MPa or more and less than 40 MPa.

When fashioning the molded product into a circular form, the diameter D thereof is preferably 20 mm or less. This is due to the fact that scattering of the alkali metal is inhibited and the activation efficiency inside the molded product is increased by reduction of the surface area of the molded product. The ratio [volume/apparent surface area], which indicates the volume of the molded product in relation to the apparent surface area, is preferably 0.1 or more and 5 or less. If the ratio thereof is less than 0.1 then activation does not adequately progress, and if the ratio thereof conversely

exceeds 5 then the shape cannot be maintained and breakdown may occur. The preferred shape of the molded product is any freely determined shape, including spherical, circular, tablet, thread, and rectangular

5   shapes.

The hot press method may also be applied to the manufacturing of the molded product, and the pressure P in relation to the powder mixture is, in this case, preferably set to 2 MPa or more. If the pressure P is

10   less than 2 MPa then the deformation strength of the molded product tends to be excessively low. The heating temperature in the hot press method is the same temperature as in the heating treatment described above. The upper limit value of the pressure P is preferably

15   40 MPa because the activation cannot adequately proceed any longer beyond that limit.

Heating process for the activation treatment

The heating process preferably involves using a reactor manufactured with pure nickel, the temperature

20   rise rate is preferably set to 200 °C/hour or more and 1,500 °C/hour or less, the heating temperature is preferably set to 600 °C or more and 1,000 °C or less, and the heating time t is preferably set to 10^{-3} hours or more and 10 hours or less, in an inert gas environment.

25   The heating process is preferably performed in advance of the high temperature heating by heating the

molded product as required to 400 °C at a temperature rise
rate Rt of 0.5 °C/minute or more and 2.0 °C/minute or less,
and subsequently holding the temperature at 400 °C for
three hours in order to maintain the shape of the molded
5   product. This heating process serves to dehydrate the
molded product in the case that water is contained
therein.

   A water-induced breakdown treatment is performed on
the molded product (including products resulting from the
10   breakdown thereof) by way of the heating process, and an
activated carbon with an average particle diameter of
about 20 μm can subsequently be obtained by sequentially
washing with hydrochloric acid, washing with water,
filtering, and drying.

15   The specific surface area of the activated carbon
obtained with such a method has a low numerical value of
1,000 m^2/g or less, and a nickel content of 20 ppm or less.

   The activated carbon obtained with the manufacturing
method of the second present invention as described above
20   can be used as a raw material for the polarizable
electrodes of an electric double-layer capacitor in the
same manner as the activated carbon obtained by the
manufacturing method of the first present invention, and
polarizable electrodes and electric double-layer
25   capacitors can be manufactured in the same manner as in
the case of the activated carbon obtained by the

manufacturing method of the first present invention is used.

<div align="center">EXAMPLES</div>

Examples of the present invention are described in

5   detail below.

The electrostatic capacity in the Examples and Comparative Examples was determined by a method in which a capacitor was charged to a final voltage of 2.5 V at a constant current per unit electrode surface area of

10   3 mA/cm^2, subjected to a supplementary charge for 30 minutes under a constant voltage of 2.5 V, and discharged at 3 mA/cm^2 after the supplementary charge had been completed, after which the capacity was calculated from the discharge gradient between that point and the

15   point at which 1.2 V to 1.0 V was reached.

The circuit was opened for one second by suspending charging after completing charging, and the charging current "I" and the voltage drop "ΔV" were obtained immediately before the opening of the circuit. The

20   internal resistance "R" was calculated according to the equation "$\Delta V = RI$".

Example 1

An optically anisotropic pitch that had been obtained by heat-treating cracked petroleum residue and had a

25   Mettler softening point of 285 °C was spun by melt blowing through a nozzle having 1,000 fiber forming holes with a

diameter of 0.2 mm in slits having a width of 2 mm, and a
mesophase pitch carbon fiber was manufactured by
infusibilization and carbonization.

   Optically anisotropic mesophase pitch fiber (50 g)
5 pulverized to a maximum length of 200 μm or less in the
   direction of the major axis, and 100 g of 95 % potassium
   hydroxide pulverized to an average particle diameter of
   1 mm or less were added to a 300 mL (milliliter) separable
   glass flask equipped with a thermometer and an agitator,
10 and the system was agitated at 10 rpm while allowing
   nitrogen to flow at 200 mL/minute. A reactor was heated
   in an oil bath, the system was heated and agitated for one
   hour at a temperature of 160 °C, the heat source was
   thereafter removed, and the system was agitated for an
15 additional hour while allowing nitrogen to flow to obtain
   a granular molded product (granulation product). The size
   of the granulation product was 20 mm or less. The
   granulation product was subsequently dehydrated under a
   reduced pressure of 1.5 Torr for five hours at a
20 temperature rise rate of 2 °C/minute to achieve a
   temperature of 300 °C.

   The crushing strength A1 (N) and the diameter B1 (cm)
   of the obtained granulation product prior to dehydration
   were measured using a crushing strength testing apparatus
25 (Autograph AG-5000B manufactured by Shimadzu Corp.,
   compression speed of 10 mm/minute), and the crushing

strength A2 (N) and the diameter B2 (cm) after dehydration
were also measured. The respective ratios [A1/B1] and
[A2/B2] were then computed by dividing the crushing
strength by the diameter (cm). The obtained values are
5   shown in Table 1.

The dehydrated granulation product was bisected at
substantially the center portion thereof; the potassium
ratio [M1 (potassium)/C1 (carbon)] of the surface layer
region of the sectioned surface thereof, and the potassium
10   ratio [M2 (potassium)/C2 (carbon)] of the center portion
were measured using a scanning electron microscope (S-
3000N, manufactured by Hitachi, Ltd.) with an energy
dispersive X-ray analyzer (EMAX, manufactured by Horiba,
Ltd.); and [M1/C1]/[M2/C2] was computed. The obtained
15   results are shown in Table 1. The measuring conditions
were SEM magnification: 100 magnifications, measured
surface area: 500 × 500 μm, measuring time: 100 seconds,
acceleration voltage: 15 kV, and atmospheric pressure:
10 Pa.

20   Next, 24 g of the granulation product obtained above
was placed in a 2-inch horizontal reactor made from
nickel and equipped with a thermometer, the air inside
the reactor was replaced with nitrogen, and the
temperature was allowed to rise to 700 °C at 200 °C/hour
25   under a nitrogen flow rate of 100 mL/minute. After the
temperature reached 700 °C, the system was held for one

hour and then cooled to room temperature for two hours
to yield granular activated carbon (activated carbon A).
Granular activated carbon (activated carbon B) was again
obtained by repeating the above operations.

5   The initially obtained activated carbon A was
separated into a powdery surface layer region of activated
carbon Aa, which was obtained by shaving off 1/5 of the
depth from the surface thereof to the center, and a center
portion activated carbon Ab with the surface layer region
10   shaved off; and the following treatment was performed.

That is, nitrogen that had passed through a distilled
water bubbler was circulated to the activated carbon for
one hour, and the activated carbon was introduced into
50 mL of water. 200 mL of 1N hydrochloric acid water was
15   added, and the system was subjected to neutralization and
wash for eight hours, continuously washed using 3 L of
distilled water, desalinated, and dried, yielding 2.7 g of
surface layer region activated carbon, and 3.4 g of center
portion activated carbon. The specific surface areas of
20   both the surface layer portion of the activated carbon and
the center portion of the activated carbon were calculated
using a specific surface area measuring apparatus (Belsorp
18, manufactured by Japan Bel, Inc.). The difference
thereof is shown in Table 1. It is apparent from the
25   difference in the specific surface areas that the

activated carbon of the present invention has small
activation nonunifomity.

Nitrogen that had passed through a distilled water
bubbler was circulated to the secondarily obtained
5   activated carbon B for one hour, and the activated carbon
was introduced into 50 mL of water. 200 mL of 1N
hydrochloric acid water was added thereto, and the system
was subjected to neutralization and wash for eight hours,
continuously washed using 3 L of distilled water,
10   desalinated, and dried, yielding 6.2 g of activated
carbon. Twenty particles of the obtained activated carbon
were extracted at random, and the Raman spectrum was
measured using a HoloLab SERIES 5000 manufactured by
Kaiser Systems, Inc. with a laser wavelength of 532 nm and
15   a laser intensity of 2 mW. The standard deviations of the
peak strengths of the graphite D band, the amorphous G
band, and the graphite G band in relation to the peak
strength of the amorphous D band are listed in Table 1,
assuming that the peak strength of the amorphous D band in
20   the Raman spectrum is set to 1.

The obtained activated carbon A or B (100 mg) was
decomposed in a wet state first with 200 mL of nitric
acid, and then with 20 mL of perchloric acid, and the
residual metal content was thereafter measured by ICP
25   spectrometry. The nickel content was 8 ppm.

The activated carbon A or B obtained was further pulverized to an average particle diameter of 5 to 20 μm to obtain pulverulent activated carbon, and a mixture comprising 80 wt% of the pulverulent activated carbon, 10
5 wt% of conductive carbon, and 10 wt% of polytetrafluoroethylene was kneaded and prepared. The kneaded product was subsequently molded into a sheet having a thickness of 300 μm by calendering, punched out into a circular shape having a diameter of 2 cm using a
10 puncher, and dried for four hours at 150 °C under reduced pressure to fabricate an electrode in a sheet form.

The obtained electrode was sequentially laminated with a collector, a polarizable electrode in a sheet form, a polypropylene unwoven fabric separator, a polarizable
15 electrode in a sheet form, and a collector member, in a stainless steel case, as shown in Fig. 1, inside a glove box with the dew point of -80 °C or lower. The polarizable electrode was thereafter impregnated with propylene carbonate containing 1 mol/L of
20 tetraethylammonium tetrafluoroborate, and the top cover of the stainless steel case was crimped and sealed using an insulating gasket made of polypropylene. A charging and discharging cycle test was conducted 10 times with a constant current until the voltage reached 2.5 V at room
25 temperature using an electric double-layer capacitor evaluation apparatus manufactured by Hioki E.E. Corp., and

the electrostatic capacity and internal resistance were
measured. The average value of the electrostatic capacity
calculated from the discharge curve by established methods
was 32.2 F/cc. The circuit was opened for one second by
5   suspending charging after complete charging, and the
internal resistance was calculated from the drop in
voltage ΔV at that time. The electrostatic capacity
retention was determined by first charging the capacitor
to 2.5 V, then charging the capacitor at a constant
10   voltage for 800 hours, thereafter calculating the
electrostatic capacity at the time of discharge, and
calculating the retention from the initial electrostatic
capacity. The results are shown in Table 1.

　　　Example 2

15   　　　Other than using a reduced pressure of 150 Torr
inside the reactor in place of the nitrogen flow in
Example 1, granulation was performed in the same manner as
Example 1, and 6.4 g of activated carbon was obtained in
the same manner as in Example 1. The nickel content in
20   the activated carbon was 9 ppm. The electrostatic
capacity, internal resistance, electrostatic capacity
retention, [A1/B1], [A2/B2], [M1/C1]/[M2/C2], and
differences in the specific surface areas were measured
for the obtained activated carbon in the same manner as
25   Example 1, and the results are shown in Table 1.

The standard deviations of the obtained peak strengths of the graphite D band, the amorphous G band, and the graphite G band in relation to the peak strength of the amorphous D band were measured in the same manner as in Example 1, and are shown in Table 1.

Comparative Example 1

Other than using 8 g of non-pulverized optically anisotropic pitch fiber having a length of 2 mm in the direction of the major axis, and 16 g of non-pulverized 95% KOH having an average particle diameter of 5 mm in place of that in Example 1, 6.8 g of activated carbon was obtained in the same manner as in Example 1. The nickel content in the activated carbon was 32 ppm. The electrostatic capacity, internal resistance, electrostatic capacity retention, [A1/B1], [A2/B2], [M1/C1]/[M2/C2], and differences in the specific surface areas were measured for the obtained activated carbon in the same manner as Example 1, and the results are shown in Table 1.

An attempt was made to measure the strength of the dehydration product at 320 °C, and determine the difference in specific surfaces areas between the surface layer region and the center portion of the activated carbon, but the contents had already melted during dehydration, and measurement was not possible.

The Raman spectrum was measured in the same manner as Example 1. Table 1 shows the standard deviations of the

obtained peak strengths of the graphite D band, the

amorphous G band, and the graphite G band in relation to

the peak strength of the amorphous D band, assuming that

the peak strength of the amorphous D band is set to 1.

5   Example 3

Other than setting the end-point temperature to 750°C

in place of that in Example 1, 6.0 g of activated carbon

was obtained in the same manner as Example 1. The nickel

content in the activated carbon was 4.4 ppm. The

10 electrostatic capacity, internal resistance, electrostatic

capacity retention, [A1/B1], [A2/B2], [M1/C1]/[M2/C2], and

differences in the specific surface areas were measured

for the obtained activated carbon in the same manner as

Example 1, and the results are shown in Table 1.

15   The standard deviations of the obtained peak

strengths of the graphite D band, the amorphous G band,

and the graphite G band in relation to the peak strength

of the amorphous D band were measured in the same manner

as in Example 1, and are shown in Table 1.

20   Example 4

Other than setting the temperature rise rate during

dehydration to 10 °C/minute, activated carbon was

manufactured with the same method as Example 1, yielding

2.5 g of activated carbon of the surface layer region,

25 3.7 g of activated carbon of the center portion, and 6.4 g

of activation carbon obtained without separating the

surface layer region and the center portion. The
electrostatic capacity, internal resistance, electrostatic
capacity retention, [A1/B1], [A2/B2], [M1/C1]/[M2/C2], and
differences in the specific surface areas were measured
5   for the obtained activated carbon in the same manner as
Example 1, and the results are shown in Table 1.

      The standard deviations of the obtained peak
strengths of the graphite D band, the amorphous G band,
and the graphite G band in relation to the peak strength
10   of the amorphous D band were measured in the same manner
as in Example 1, and are shown in Table 1.

      Comparative Example 2

      A mixture of 300 g of non-pulverized optically
anisotropic pitch having a length of 2 mm in the direction
15   of the major axis and 600 g of 95% potassium hydroxide in
flake form were loaded into a vertical reactor that was
made of nickel, had a diameter of 6 inches, and was
equipped with a thermometer, and the mixture was allowed
to stand inside an electric furnace. The system was
20   heated to 730 °C from room temperature at a temperature
rise rate of 200 °C/hour while allowing a flow of nitrogen
into the upper space of the reactor at a rate of
100 mL/minute, and was held for three hours. The system
was removed from the electric furnace and cooled to
25   300 °C, the nitrogen gas was switched to carbondioxide
gas, and cooling was continued to room temperature. The

height at loading was 25 cm, but was 30 cm after activation, and traces of foaming were observed up to a height of about 80 cm from the bottom.

When the reactor was opened after activation, a pale flash was generated on the surface of the blackened activated product and on the inner surface of the reactor, the system turned red, and thereafter violently combusted while scattering matter and producing a large quantity of white smoke. Combustion continued for two hours.

The activated product was dissolved in a quantity of water triple that of the activated product and removed, 2.5 L of 0.6 N hydrochloric acid water was added, neutralization was repeated three times, and the product was thereafter washed five times with 2.5 L of distilled water. The activated carbon after drying was 249 g, and the nickel content in the activated carbon was 1,050 ppm.

TABLE 1

	Example 1	Example 2	Example 3	Example 4	Comparative Example 1
Electrostatic capacity (F/cc)	32.2	31.3	30.8	31.0	27.4
Electrostatic capacity retention (%)	91.4	90.3	88.6	90.6	62.2
Internal resistance (Ω)	16	14	14	16	27
Before Dehydration [A1/B1] (N/cm)	202			202	Not measurable
After Dehydration [A2/B2] (N/cm)	108			185	Not measurable
Potassium Ratio [M1/C1]/[M2/C2]	1.6			2.6	Not measurable
Specific surface area Difference (m²/g)	80			180	
Standard Deviation of Each Peak Strength Graphite D Band	0.0299	0.0289	0.0275	0.0312	0.0603
Amorphous G Band	0.0257	0.0262	0.0283	0.0306	0.0362
Graphite G Band	0.0304	0.0306	0.0312	0.0322	0.0343

Reference Example 1: Manufacture of Composite Product
1

50 g of the carbonized carbonaceous material powder,
which is obtained by dry-distilling and carbonizing
coconut shells at 900 °C with a length of 20 μm or less,
and 100 g of 95% potassium hydroxide pulverized to an
average particle diameter of 1 mm or less were added to a
300 mL (milliliters) separable glass flask equipped with a
thermometer and an agitator; and the system was agitated
at 10 rpm while allowing nitrogen to flow at
200 mL/minute. The separable flask was heated in an oil
bath, the system was heated and agitated for one hour at a

temperature of 160 °C inside the container, the heat
source was thereafter removed, and the system was agitated
for an additional hour while allowing nitrogen to flow to
obtain a composite product 1.

5   Example 5

The composite product (24 g) prepared in reference
example 1 was placed in a 2-inch horizontal reactor made
from nickel and equipped with a thermometer, the air
inside the reactor was replaced with nitrogen, and the
10   temperature was raised to 700 °C at 200 °C/hour under a
nitrogen flow rate of 100 mL/minute. After the
temperature reached 700 °C, the system was held for one
hour and then cooled to room temperature for two hours.
Nitrogen that had passed through a distilled water bubbler
15   was circulated for one hour, and the activated carbon was
introduced into 50 mL of water. 200 mL of 1N hydrochloric
acid water was added, and the system was subjected to
neutralization and wash for eight hours, then continuously
washed using 3 L of distilled water, desalinated, and
20   dried, yielding 5.2 g activated carbon.

The obtained activated carbon (100 mg) was decomposed
in a wet state first with 200 mL of nitric acid, and then
with 20 mL of perchloric acid, and the residual metal
content was thereafter measured by ICP spectrometry. The
25   nickel content was 6.7 ppm.

The activated carbon was further pulverized to an
average particle diameter of 5 to 20 μm to obtain
pulverulent activated carbon, and a mixture comprising
80 wt% of the pulverulent activated carbon, 10 wt% of
5   conductive carbon, and 10 wt% of polytetrafluoroethylene
was kneaded and prepared. The kneaded product was
subsequently molded into a sheet having a thickness of
300 μm by calendering, punched out into a circular shape
having a diameter of 2 cm using a puncher, and dried for
10   four hours at 150 °C under reduced pressure to fabricate
an electrode in a sheet form.

      This was sequentially laminated with a collector, a
polarizable electrode in a sheet form, a polypropylene
unwoven fabric separator, a polarizable electrode in a
15   sheet form, and a collector, in a stainless steel case, as
shown in Fig. 1, inside a glove box with the dew point of
-80 °C or lower. The polarizable electrode was thereafter
impregnated with propylene carbonate containing 1 mol/L of
tetraethylammonium tetrafluoroborate, and the top cover of
20   the stainless steel case was crimped and sealed using an
insulating gasket made of polypropylene. A charging and
discharging cycle test was conducted 10 times with a
constant current until the voltage reached 2.5 V at room
temperature using an electric double-layer capacitor
25   evaluation apparatus manufactured by Hioki E.E. Corp., and
the electrostatic capacity, electrostatic capacity

retention, internal resistance were measured. The average
value of the electrostatic capacity calculated from the
discharge curve by an established method was 21 F/cc. The
circuit was opened for one second by suspending charging

5   after complete charging, and the internal resistance was
calculated from the drop in voltage ΔV at that time. The
results are shown in Table 2.

Reference Example 2: Manufacture of Composite Product
2

10   Other than using a reduced pressure of 150 Torr
inside the reactor in place of the nitrogen flow in
Reference Example 1, a composite product 2 was obtained in
the same manner as reference Example 1.

Example 6

15   Other than using the composite product 2 in place of
the composite product 1 in Example 1, 5.3 g of activated
carbon was obtained in the same manner as Example 5. The
nickel content in the activated carbon was 3.77 ppm. The
results of measuring the electrostatic capacity,

20   electrostatic capacity retention, and internal resistance
are shown in Table 2.

Comparative Example 3

6.8 g of activated carbon was obtained in the same
manner as Example 1, except that 8 g of coconut shell

25   powder with an average particle diameter of 1 mm, obtained
by dry distilling and carbonizing coconut shells at

900 °C, was used together with 16 g of non-pulverized 95 %

potassium hydroxide in place of the composite product 1 in

Example 6.   The nickel content in the activated carbon was

111 ppm. The results of measuring the electrostatic

5   capacity, electrostatic capacity retention, and internal

resistance are shown in Table 2.

Table 2

	Electrostatic capacity (F/cc)	Electrostatic capacity retention (%)	Internal resistance (Ω)
Example 5	21	89.3	16
Example 6	23	90.1	14
Comparative Example 3	19	70.3	27

Reference Example 3: Manufacture of Composite Product

10   3

BELLPEARL manufactured by Kanebo, Ltd. was dry

distilled at 500 °C; 50 g of the carbon pulverized to

30 μm or less, and 100 g of 95% potassium hydroxide

pulverized to an average particle diameter of 1 mm or less

15   were added to a 300 mL (milliliters) separable glass flask

equipped with a thermometer and an agitator; and the

system was agitated at 10 rpm while allowing nitrogen to

flow at 200 mL/minute. The separable flask was heated in

an oil bath, the system was heated and agitated for one

20   hour at a temperature of 160 °C inside the container, the

heat source was thereafter removed, and the product was
agitated for an additional hour while allowing nitrogen to
flow to obtain a composite product 3.

Example 7

5   The composite product 3 (24 g) was placed in a 2-inch
horizontal reactor made from nickel and equipped with a
thermometer, the air inside the reactor was replaced with
nitrogen, and the temperature was raised to 700 °C at
200 °C/hour under a nitrogen flow rate of 100 mL/minute.

10   After the temperature reached 700 °C, the system was held
for one hour and then cooled to room temperature for two
hours. Nitrogen that had passed through a distilled water
bubbler was circulated for one hour, and was then added to
50 mL of water. 200 mL of 1N hydrochloric acid water was

15   added, and the system was subjected to neutralization and
wash for eight hours, then continuously washed using 3 L
of distilled water, desalinated, and dried, yielding 6.2 g
activated carbon.

       100 mg of the resulting obtained activated carbon was

20   decomposed in a wet state first with 200 mL of nitric
acid, and then with 20 mL of perchloric acid, and the
residual metal content was thereafter measured by ICP
spectrometry. The nickel content was 8 ppm.

       The activated carbon was further pulverized to an

25   average particle diameter of 5 to 20 μm to obtain
pulverulent activated carbon, and a mixture comprising

80 wt% of the pulverulent activated carbon, 10 wt% of
conductive carbon, and 10 wt% of polytetrafluoroethylene
was kneaded and prepared. The kneaded product was
subsequently molded into a sheet having a thickness of

5   300 µm by calendering, and punched out into a circular
shape having a diameter of 2 cm using a puncher. The
product was dried for four hours at 150 °C under reduced
pressure to fabricate an electrode in a sheet form.

This was sequentially laminated with a collector, a

10 polarizable electrode in a sheet form, a polypropylene
unwoven fabric, a polarizable electrode in a sheet form,
and a collector, in a stainless steel case, as shown in
Fig. 1, inside a glove box with the dew point of -80°C or
lower. The polarizable electrode was thereafter

15 impregnated with propylene carbonate containing 1 mol/L of
tetraethylammonium tetrafluoroborate, and the top cover of
the stainless steel case was crimped and sealed using an
insulating gasket made of polypropylene. A charging and
discharging cycle test was conducted 10 times with a

20 constant current until the voltage reached 2.5 V at room
temperature using an electric double-layer capacitor
evaluation apparatus manufactured by Hioki E.E. Corp., and
the electrostatic capacity, electrostatic capacity
retention, and internal resistance were measured. The

25 average value of the electrostatic capacity calculated
from the discharge curve by established methods was

26 F/cc. The circuit was opened for one second by
suspending charging after complete charging, and the
internal resistance was calculated from the drop in
voltage ΔV at that time. The results are shown in Table
5   3.

Reference Example 4: Manufacture of Composite Product
4

Other than using a reduced pressure of 150 Torr
inside the reactor in place of the nitrogen flow in
10   reference example 3, a composite product 4 was obtained in
the same manner as reference example 3.

Example 8

Other than using the composite product 4 in place of
the composite product 3 in Example7, 6.4 g of activated
15   carbon was obtained in the same manner as Example 7. The
nickel content in the activated carbon was 9 ppm. The
results of measuring the electrostatic capacity,
electrostatic capacity retention, and internal resistance
are shown in Table 3.

20   Comparative Example 4

Other than using 8 g of the carbonized phenol resin
with an average particle diameter of 0.1 mm and 16 g of
non-pulverized 95% potassium hydroxide in place of the
composite product 3 in Example 7, 6.8 g of activated
25   carbon was obtained in the same manner as Example 8. The
nickel content in the activated carbon was 32 ppm. The

results of measuring the electrostatic capacity, electrostatic capacity retention, and internal resistance are shown in Table 3.

Example 9

5   Other than setting the end-point temperature to 750 °C in place of that in Example 7, 6.0 g of activated carbon was obtained in the same manner as Example 7. The nickel content in the activated carbon was 4.4 ppm. The results of measuring the electrostatic capacity, 10   electrostatic capacity retention, and internal resistance are shown in Table 3.

Example 10

A composite product was manufactured using the carbonized phenol resin fiber in place of the phenol resin 15   carbide pulverized product in Reference Example 3. Other than using this in place of that in Example 7, 5.4 g of activated carbon fiber was obtained in the same manner as Example 8. The nickel content in the activated carbon was 2.1 ppm, the system was pulverized in a mixer, and the 20   results of measuring the electrostatic capacity, electrostatic capacity retention, and internal resistance are shown in Table 3.

Reference Example 5: Manufacture of Composite Product 5

25   Sulfuric acid (200 g) was added to 100 g of ethylene-vinyl alcohol copolymer, and agitated for three hours at

140 °C. This was poured in 1,000 g of ice water and
rinsed, and the acid condensation product was filtered
out, washed again with 10 L of distilled water, and dried
to yield 28 g of acid condensation product. The product

5 was mixed with 56 g of potassium hydroxide in accordance
with Reference Example 3 to obtain a composite product 5.

Example 11

Other than replacing the phenol resin in Example 7
with the composite product 5 obtained in Reference Example

10 5, 4.7 g of activated carbon was obtained in the same
manner as Example 7. The nickel content in the activated
carbon was 1.7 ppm. The results of measuring the
electrostatic capacity, electrostatic capacity retention,
and internal resistance are shown in Table 3.

15

Table 3

	Electrostatic capacity (F/cc)	Electrostatic capacity retention (%)	Internal resistance (Ω)
Example 7	26.0	90.5	14
Example 8	26.5	89.6	13
Comparative Example 4	25.0	66.1	12
Example 9	26.3	90.1	13
Example 10	26.7	89.3	12
Example 11	24.1	88.7	20

Example 12

A ball mill composed of nylon resin with an internal volume of 100 L was loaded to 50 % capacity with alumina balls having a diameter of 30 mm. The interior of the

5 ball mill was replaced with air having a low dew point of -17 °C, and 25 kg of 95 % potassium hydroxide in flake form and 0.75 kg of mesophase pitch carbon fiber (3wt%/95% potassium hydroxide) were loaded. A uniform pulverized product having an average particle diameter of 10 μm and

10 excellent fluidity was obtained without bridge formations by operating the ball mill for two hours at a circumferential speed of 1 m/sec.

Mesophase pitch carbon fiber (0.63 kg) pulverized so that the maximum length in the axial direction was 200 μm

15 or less, and 1.3 kg of 95% potassium hydroxide to which the mesophase pitch carbon fiber pulverized with the ball mill had been added, were placed in a batch-type, externally heated rotary kiln composed of nickel with a diameter of 400 mm and a length of 300 mm, and equipped

20 with a thermometer, and the rotary kiln was rotated at 30rpm under a reduced pressure of 0.3 Torr (95% potassium hydroxide/mesophase pitch carbon fiber = 1.8 weight ratio).

The mixture of mesophase pitch carbon fiber and

25 potassium hydroxide was heated to raise the temperature from room temperature to 100 °C at a rate of 0.5 °C/minute,

and while maintaining the rotational speed of the rotary
kiln and the reduced pressure condition, the power was
cut, and the system was allowed to cool, yielding a
granular product. The size of the granular product was 16
5   mm or less.

    While rotating at 30 rpm using the same rotary kiln,
the temperature of the granulation product was raised to
320 °C from room temperature at a rate of 0.5 °C/minute
under reduced pressure of 0.3 Torr, and this temperature
10 was maintained for one hour to dehydrate the product.

    The granular product obtained from dehydration was
classified into fractions with particle diameters of 1 mm
or less, 1 to 2.4 mm, 2.4 to 4.8 mm, 4.8 to 8 mm, 8 to 11
mm, 11 to 16 mm, and 16 mm or more. The results of
15 measuring the 95% potassium hydroxide/mesophase pitch
carbon fiber weight ratios are shown in Table 4.

<div align="center">Table 4</div>

Particle diameter (mm)	Composition ratio	Composition ratio variability (%)
< 1	1.85	+3
1 to 2.4	1.79	−0.6
2.4 to 4.8	1.79	−0.6
4.8 to 8	1.79	−0.6
8 to 11	1.77	−1.7
11 to 16	1.75	−2.8
16<	1.73	−3.9

An externally heated rotary kiln-type electric
furnace comprising a thermometer, a nitrogen inlet, and a
gas exhaust port having a water trap, and having a
temperature-variable activation zone (activation zone
5   inside diameter of 100 mm, and internal volume of 400 mL)
was used as the activation furnace. The granular product
(50 g) after dehydration was loaded into the activation
zone under a nitrogen flow. The temperature of the
activation zone was raised from room temperature to 730 °C
10   at a temperature rise rate of 200 °C/hour while allowing
nitrogen to flow at 300 mL/minute, and after reaching the
predetermined temperature, the temperature was held for
three hours. The system was thereafter cooled to 50 °C or
less under a nitrogen flow, and the activated carbon
15   material obtained by activation was then treated under a
flow of mixed gas of carbon dioxide gas and water vapor to
deactivate the residual metal potassium.

The above activation operations were repeated to
manufacture activated carbon, and the activated carbon was
20   washed and fabricated into an electrode in a sheet form in
the same manner as Example 1. An electric double-layer
capacitor was fabricated with the same operations as
Example 1, and when the electrostatic capacity was
measured, the average was 32 F/cc, and the variation
25   thereof was small as 32 ± 0.3 F/cc, resulting in a uniform

electric double-layer capacitor. The nickel and iron
contents were respectively 5 ppm and 3 ppm.

   The electrostatic capacity, internal resistance,
electrostatic capacity retention, [A1/B1], [A2/B2],
[M1/C1]/[M2/C2], and differences in the specific surface
areas were measured for the obtained activated carbon in
the same manner as in Example 1, and the results are shown
in Table 7.

   The standard deviations of the obtained peak
strengths of the graphite D band, the amorphous G band,
and the graphite G band in relation to the peak strength
of the amorphous D band were measured in the same manner
as in Example 1, and are shown in Table 7.

   Example 13

   20 kg of the flaky 95% potassium hydroxide and 1.0 kg
of mesophase pitch carbon fiber (5wt%/95% potassium
hydroxide) were loaded, and other than pulverizing the
flaky potassium hydroxide, a granular product after
dehydration was obtained in the same manner as Example 12.
The obtained granular product was similarly separated into
categories of particle diameters, and the results are
shown in Table 5.

Table5

Particle diameter (mm)	Composition ratio	Composition ratio variability (%)
< 1	1.85	+3
1 to 2.4	1.80	0
2.4 to 4.8	1.79	−0.6
4.8 to 8	1.79	−0.6
8 to 11	1.78	−1.1
11 to 16	1.76	−2.2
16 <	1.73	−3.9

An electric double-layer capacitor was fabricated in
the same manner as Example 12, and when the electrostatic
capacity was measured, the average was 32.3 F/cc, and the
variation thereof was small at 32.3 ± 0.3 F/cc, resulting
in a uniform electric double-layer capacitor. The nickel
and iron contents were respectively 4 ppm and 3 ppm.

When conducted in the same manner as Example 12
without adding mesophase pitch carbon fiber in advance,
the results noted in Table 6 were obtained.

Table 6

Particle diameter (mm)	Composition ratio	Composition ratio variability (%)
< 1	2.11	+17
1 to 2.4	1.61	−10.6
2.4 to 4.8	1.66	−8.8
4.8 to 8	1.74	−3.3
8 to 11	1.78	−1.1
11 to 16	1.76	−2.2
16 <	1.73	−3.9

An electric double-layer capacitor was fabricated in
5　the same manner as Example 12. The nickel and iron
contents were respectively 9 ppm and 7 ppm, and when the
electrostatic capacity was measured, the average was
31.1 F/cc, and the variation thereof was 31.1 ± 0.8 F/cc.

The electrostatic capacity, internal resistance,
10　electrostatic capacity retention, [A1/B1], [A2/B2],
[M1/C1]/[M2/C2], and differences in the specific surface
areas were measured for the obtained activated carbon in
the same manner as in Example 1, and the results are shown
in Table 7.

15　The standard deviations of the obtained peak
strengths of the graphite D band, the amorphous G band,
and the graphite G band in relation to the peak strength
of the amorphous D band were measured in the same manner
as in Example 1, and are shown in Table 7.

Example 14

After granulation and dehydration were performed in
the same manner as Example 12, an externally heated rotary
kiln-type electric furnace (SUS304) that comprised a
continuous feeding device for the granular product after
dehydration, a thermometer, a nitrogen inlet, and a gas
exhaust port having a water trap, and had a temperature-
variable activation zone (activation zone inside diameter
of 300 mm, and activation length of 6,000 mm, and internal
volume of 416 L) was used as the activation furnace, and
activation treatment was performed using the continuous
process.

Operation was started by rotating the rotary kiln at
a rotational speed of 2 rpm (circumferential speed of
2 m/minute). The activation zone was adjusted to a
predetermined temperature gradient while allowing nitrogen
to flow at a rate of 5.5 L/minute, and the granular
product after dehydration was continuously fed at a rate
of 2.7 kg/hour. The activation reaction progressed from
room temperature to 730 °C at a temperature rise rate of 1
°C/minute. The heating time to 700 °C or more was four
hours, and the residence time inside the rotary kiln was
24.2 hours. After cooling by passing through the cooling
zone of the rotary kiln, the activated product
continuously discharged was stored in a discharge
receptacle. The activated product was removed from the

reactor and treated under a flow of carbon dioxide gas to
deactivate the residual metal potassium.

    A mixture comprising 80 wt% of the pulverulent
activated carbon in which the activated product was
5   pulverized to an average particle diameter of 5 to 20 μm,
10 wt% of conductive carbon, and 10 wt% of
polytetrafluoroethylene was kneaded and prepared.   The
kneaded product was subsequently molded into a sheet
having a thickness of 300 μm by calendering, and punched
10 out into a circular shape having a diameter of 2 cm using
a puncher.   The product was dried for four hours at 150 °C
under reduced pressure to fabricate an electrode in a
sheet form.

    This was sequentially laminated with a collector
15 member, a polarizable electrode in a sheet form, a
polypropylene unwoven fabric separator, a polarizable
electrode in a sheet form, and a collector on a stainless
steel cover inside a glove box with the dew point of -80°C
or lower, the polarizable electrode was thereafter
20 impregnated with a propylene carbonate solution containing
1 mol/L of tetraethylammonium tetrafluoroborate, and the
stainless steel top cover was crimped and sealed using an
insulating gasket made of polypropylene, resulting in the
fabrication of an electric double-layer capacitor such as
25 that shown in Fig. 1.   A charging and discharging cycle
test was conducted 10 times with a constant current until

the voltage reached 2.5 V at room temperature using an
electric double-layer capacitor evaluation apparatus
manufactured by Hioki E.E. Corp., and the electrostatic
capacity was measured. The average value of the
5   electrostatic capacity calculated from the discharge curve
by established methods was 33.0 F/cc.

The electrostatic capacity, internal resistance,
electrostatic capacity retention, [A1/B1], [A2/B2],
[M1/C1]/[M2/C2], and differences in the specific surface
10   areas were measured for the activated carbon obtained in
the same manner as in Example 1, and the results are shown
in Table 7.

The standard deviations of the obtained peak
strengths of the graphite D band, the amorphous G band,
15   and the graphite G band in relation to the peak strength
of the amorphous D band were measured in the same manner
as in Example 1, and are shown in Table 7.

Example 15

Other than allowing the activation reaction in
20   Example 14 to progress from room temperature to 730°C at a
temperature increase rate of 2 °C/minute, and setting the
heating time to 700°C or more to 2.4 hours and the
residence time inside the rotary kiln to 14.5 hours, the
same operations as in Example 14 were performed. The
25   specific surface area and the pore volume of the product
were respectively 1,084 m^2/g and 0.48 cc/g. The potassium,

nickel, and iron contents were respectively 50 ppm,
0.2 ppm, and 1.5 ppm. The electrostatic capacity was
31.5 F/cc.

The electrostatic capacity, internal resistance,
electrostatic capacity retention, [A1/B1], [A2/B2],
[M1/C1]/[M2/C2], and differences in the specific surface
areas were measured for the activated carbon obtained in
the same manner as in Example 1, and the results are shown
in Table 7.

The standard deviations of the obtained peak
strengths of the graphite D band, the amorphous G band,
and the graphite G band in relation to the peak strength
of the amorphous D band were measured in the same manner
as in Example 1, and are shown in Table 7.

Reference Example 6

An optically anisotropic pitch that had been obtained
by heat-treating cracked petroleum residue and had a
Mettler softening point of 285 °C was spun by melt blowing
through a nozzle having 1,000 fiber forming holes with a
diameter of 0.2 mm in slits having a width of 2 mm, and a
mesophase pitch carbon fiber was manufactured by
infusibilization and carbonization.

A carbonaceous material (0.74 kg) in which the
mesophase carbon fiber fabricated in the method described
above was pulverized to a maximum length of 200 μm or less
in the direction of the major axis, and 1.26 kg of 95%

potassium hydroxide pulverized to an average particle
diameter of 100 μm or less were placed in a stainless
steel, double cone-type mixer having a diameter of 800 mm
and equipped with a thermometer, and the double cone-type
5 mixer was rotated at 16 rpm under a reduced pressure of
3.0 Torr. The mixture of mesophase pitch carbon fiber and
potassium hydroxide was heated to raise the temperature
from room temperature to 130 °C at a rate of 1.0 °C/minute,
and the system was then allowed to cool while the
10 rotational speed of the rotary kiln and the reduced
pressure condition were maintained, yielding a granulation
product. The size of the granulation product was 10 mm or
less.

     Example 16

15   The granulated product (0.5 kg) obtained in Reference
Example 6 was placed in the rotary kiln that was made of
nickel, had a diameter of 400 mm and a length of 200 mm,
was equipped with a thermometer, and served as a
dehydration apparatus. The pressure was held at 3 Torr,
20 and the kiln was rotated at 16 rpm while the temperature
was raised from room temperature to 300 °C at a rate of
2.0 °C/minute. The system was immediately cooled upon
reaching 300 °C while the pressure and rotational speed
were kept unchanged, and the granulated product was then
25 removed. It was confirmed by visual observation that the

granulation product had been dehydrated while maintaining the solid state.

The electrostatic capacity, internal resistance, electrostatic capacity retention, [A1/B1], [A2/B2],

5   [M1/C1]/[M2/C2], and differences in the specific surface areas were measured for the obtained activated carbon in the same manner as in Example 1, and the results are shown in Table 7.

The standard deviations of the obtained peak

10   strengths of the graphite D band, the amorphous G band, and the graphite G band in relation to the peak strength of the amorphous D band were measured in the same manner as in Example 1, and are shown in Table 7.

TABLE 7

	Example 12	Example 13	Example14	Example 15	Example16
Electrostatic capacity (F/cc)	32.0	32.3	33.0	31.5	31.5
Electrostatic capacity retention (%)	91.2	90.6	91.8	90.9	90.3
Internal resistance (Ω)	14	15	14	16	16
Before Dehydration [A1/B1] (N/cm)	180	189	180	180	170
After Dehydration [A2/B2] (N/cm)	96	99	96	96	88
Potassium Ratio [M1/C1]/[M2/C2]	1.6	1.6	1.6	1.6	1.7
Specific surface area Difference (m²/g)	70	80	80	70	90
Standard Deviation of Each Peak Strength					
Graphite D Band	0.0295	0.0301	0.0303	0.0293	0.0297
Amorphous G Band	0.0276	0.0269	0.0271	0.0262	0.0271
Graphite G Band	0.0312	0.0311	0.0311	0.0308	0.0313

15

Example 17

0.2 kg of granulation product obtained by repeating Reference Example was placed in an oblong Pyrex glass flask serving as a dehydration apparatus with a 500 mL capacity and equipped with a thermometer. The pressure was held at 3 Torr, and the flask was rotated at 16 rpm while the temperature was raised from room temperature to 300 °C at a rate of 2.0 °C/minute. The system was immediately cooled upon reaching 300°C while the pressure and rotational speed were kept unchanged, and the granulation product was then removed. It was confirmed in the same manner as Example 1 that the granulation product had been dehydrated while maintaining the solid state.

Examples 18 and 19, Comparative Examples 5 to 7

Other than changing the pressure inside the container and the temperature rise rate as shown in Table 7, dehydration was performed with the same method as in Example 17. The results are shown in Table 8. It is apparent from these results that dehydration can be performed while maintaining the solid state of the mixture of mesophase pitch carbon fiber and potassium hydroxide by combining the pressure inside the container with the temperature rise rate for the dehydration treatment.

Table 8

	Container Pressure (Torr)	Temperature Rise Rate [°C/minute]	State during Dehydration Treatment
Example 18	10	0.8	Solid State Maintained
Emample 19	1	10	Solid State Maintained
Comparative Example 5	10	2	Melted
Comparative Example 6	52	0.5	Melted
Comparative Example 7	3	8	Melted

Example 20

5   0.7 kg of pitch in which the mesophase pitch carbon
fiber fabricated in Reference Example 6 was pulverized to
a maximum length of 200 μm or less in the direction of the
major axis, and 1.3 kg of 95% potassium hydroxide
pulverized to an average particle diameter of 1 mm or less
10   were loaded into a batch-type, externally-heated rotary
kiln that was made from nickel, had a diameter of 400 mm
and a length of 300 mm, and was equipped with a
thermometer. The rotary kiln was rotated at 30 rpm under
a reduced pressure of 0.3 Torr. The mixture of mesophase
15   pitch carbon fiber and potassium hydroxide was heated from
room temperature to 100 °C at a rate of 0.5 °C/minute, the
power was cut while the rotational speed of the rotary
kiln and the reduced pressure condition were kept

unchanged, and the system was allowed to cool, yielding a
granulation product. The size of the granulation product
was 10 mm or less.

 While rotating at 30 rpm using the same rotary kiln,
5 the temperature of the granulation product was raised to
320°C from room temperature at a rate of 0.5 °C/minute
under reduced pressure of 0.3 Torr, the temperature was
maintained for one hour, and the product was dehydrated.

 The activation furnace was an externally-heated,
10 rotary kiln-type electric furnace that was made from
nickel, that comprised a thermometer, a nitrogen inlet,
and a gas exhaust port having a water trap, and that had a
temperature-variable activation zone (activation zone
inside diameter of 100 mm, internal volume of 400 mL
15 (milliliters)), and an activated carbon loading zone
(loading zone inside diameter of 28 mm, and internal
volume of 230 mL) as a sorbent material (adsorbent). The
dehydration product (50 g) was loaded into the activation
zone under a nitrogen flow, and 10 g (loading capacity
20 20 mL) of coconut shell activated carbon (GG4/8,
manufactured by Kuraray Chemical Co., Ltd.) was loaded so
as not to leave a cavity.

 While allowing nitrogen to flow at a rate of 300
mL/minute (activation zone residence time of 4.0 seconds,
25 and gas linear velocity of 8.3 mm/second), the temperature
of the activation zone was raised from room temperature to

730°C, the temperature of the loading zone was raised to
650°C at a temperature rise rate of 200 °C/hour, and the
system was held for three hours after reaching the
predetermined temperature. The system was thereafter
5   cooled to 50 °C or less under a nitrogen flow, the
activated carbon used to adsorb the alkali metal and the
activated carbon obtained by activation were removed,
potassium was obtained by titration with 0.1N hydrochloric
acid, and the residual quantity of potassium was
10   determined by quantifying the hydrogen generated by adding
water. Metal potassium, strong alkali salts, and weak
alkali salts were contained in the potassium obtained by
titration, and scattering of the metal potassium and
strong alkali salt was a problem.
15   As a result of analysis, generation of hydrogen due
to residual potassium was not observed from either the
activated carbon used in sorption or the activated carbon
obtained by activation, and the weak alkali salts that are
assumed to originate in potassium carbonate in the water
20   trap were only detected at 0.1 mol% of the loaded
potassium content, indicating that the potassium scattered
from the activation zone was captured in the adsorbent
loading zone and deactivated.
        Example 21
25   12 g of the same dehydrated product as in Example
20 was used, and the activation furnace was an electric

furnace equipped with a thermometer, a nitrogen inlet, and
a gas exhaust port having a water trap, and had a built-in
reaction tube made from nickel with an internal diameter
of 42 mm with an activation zone and an adsorbent loading

5   zone. The same coconut shell activated carbon 5 g
(loading capacity 10 mL) used in Example 1 was loaded into
the adsorbent loading zone, and while allowing nitrogen to
flow at a rate of 300 mL/minute (the residence time of 2.0
seconds in the activation zone, and gas linear velocity of

10 3.6 mm/second), the temperature of the activation zone was
raised from room temperature to 730 °C, the temperature of
the adsorbent loading zone was raised to 700 °C at a
temperature rise rate of 200 °C/hour, and the system was
held for an hour after reaching the predetermined

15 temperature.

The system was thereafter cooled to 50 °C or less
under a nitrogen flow, and the activated product and the
activated carbon for adsorption were removed.
Determinations were made as to the potassium calculated by

20 titration with 0.1N hydrochloric acid, and the residual
quantity of potassium calculated by quantifying the
hydrogen generated by the addition of water, but there was
no observable generation of hydrogen due to the metal
potassium residue from either the activated product or the

25 activated carbon for adsorption, and the weak alkali salts
that were assumed to originate in potassium carbonate in

the water trap were only detected at 0.08 mol% of the
loaded potassium, indicating that the potassium scattered
from the activation zone was captured in the activated
carbon zone for adsorption and stabilized.

5   Examples 22 to 25, Comparative Examples 8 to 10

Other than changing the nitrogen flow rate,
activation zone temperature, activation zone for
adsorption temperature, and type and quantity of activated
carbon for adsorption, activation operations were
10   performed with the same method as in Example 21.   The
obtained results are shown in Table 9.

Table 9

	Examples				Comparative Examples		
	22	23	24*	25	8	9	10*
Nitrogen flow (ml/minute)	120	350	200	150	500	600	900
Contact time (seconds)	5.0	1.7	3.0	4.5	0.4	0.3	0.3
Line speed (mm/minute)	1.4	4.2	2.4	1.8	6.0	7.2	10.8
Activation zone temperature (°C)	730	800	700	730	730	750	730
Sorption zone temperature (°C)	410	700	450	700	400	500	250
Existence of hydrogen generation	No	No	No	No	Yes	Yes	Yes
Strong alkali in the trap	Not Detected	Not Detected	Not Detected	Not Detected	0.5**	0.6**	1.2**

* Using coal activated carbon

15   ** Molar percent in relation to the loaded alkali

       In the cases of Comparative Examples 8 to 10, in
   which the contact time between the activated carbon for
   adsorption and nitrogen gas was less than 0.5 seconds, as
   shown in Table 9, hydrogen was generated when activated
5 carbon material and the activated carbon for adsorption
   were washed with water, so it is apparent that the metal
   potassium was held in these in an active state. It is
   particularly apparent from the results of Comparative
   Example 10 that the quantity of alkali metal that was not
10 deactivated increased when the adsorption zone temperature
   was less than 300 °C.
       In contrast to the above, the results of Examples 22
   to 25, which have contact times greater that exceed
   0.5 seconds, and adsorption zone temperatures that are
15 between 300 and 800 °C, indicate that hydrogen was not
   generated and that strong alkalis were not detected in the
   trap, so it is apparent that the alkali metal in vapor
   form that was generated during the heat treatment of the
   activation treatment was deactivated by the activated
20 carbon for adsorption.
       Example 26
       (1) Three grams (W_1) of a carbonaceous material
   powder (atomic ratio H/C = 0.2) with an average particle
   diameter of 15 μm, obtained using mesophase pitch as the
25 starting material, and 5.7 g (W_2) of 95%-pure KOH powder
   having an average particle diameter of 50 μm and serving

as an alkali metal-containing activator powder were
thoroughly mixed at room temperature (20 °C) with the aid
of a cutting mixer to obtain a powder mixture. The ratio
of both weights (W_2/W_1) in this powder mixture was 1.9.

5   (2) The powder mixture was placed in a PTFE container
inside of an electric furnace at 200 °C, and heating
treatment was performed for 24 hours under a nitrogen flow
(linear velocity = 20 cm/minute), yielding a solid
product.

10   (3) After heating, the uncooled solid product was
pressed under 20 MPa in a tablet molding machine to
fashion a molded tablet product in table form with a
diameter of 10 mm and a thickness of 2 mm.

        (4) The molded tablet product obtained was placed in
15 a reactor that was made from pure nickel, and the
temperature was first raised to 400°C at a temperature
rise rate of 0.5°C/minute under a nitrogen flow (linear
velocity 20 cm/minute), then held at 400°C for three hours,
raised to 730°C at a temperature rise rate of 200 °C/hour,

20 and subsequently held for three hours at 730 °C. The
shape of the product remained unchanged before and after
the high heat treatment subjected to this type of high
temprature heating did not change from that of the molded
product before and after the high heat treatment.

25   (5) The heat-treated product in tablet form was
broken down by water, sequentially washed with 0.1N

hydrochloric acid and with water, filtered, and dried to
obtain an activated carbon with an average particle
diameter 20 μm as the activated carbon of Example 26.

Example 27

Other than setting the pressure P applied during the
molding of the tablet product to 5 MPa, an activated
carbon having an average particle diameter of 20 μm was
obtained as the activated carbon of Example 27 by the same
method as the one in Example 26. In this case, partial
melting in the heat-treated product was observed during
the same high temperature heating as that performed in
step (4) of Example 26, but the melted portion did not
adhere to the reactor. It was possible to remove this
treatment product from the reactor by washing out with
water.

Example 28

Other than setting the average particle diameter of
the carbonaceous material powder to 20 μm, a molded tablet
product having a diameter of 10 mm and a thickness of 2 mm
was obtained as the activated carbon of Example 28 by
conducting hot pressing under conditions that
corresponding to a heating temperature of 260 °C, an
applied pressure of 2 MPa, and an applied pressure holding
time of 60 seconds, using the same powder mixture as in
Example 26.

Comparative Example 11

(1) Three grams (W_1) of a carbonaceous material powder (atomic ratio H/C = 0.2) with an average particle diameter of 20 μm, obtained using mesophase pitch as the starting material, and 5.7 g (W_2) of 95%-pure KOH powder having an average particle diameter of 50 μm and serving as the alkali metal activator powder were sufficiently mixed at room temperature (20 °C) with the aid of a cutting mixer to obtain a powder mixture. The ratio of both weights [W_2/W_1] in this powder mixture was 1.9.

(2) The powder mixture obtained was placed in a reactor that was made from pure nickel so as to have a height of 5 mm, the reactor containing the powder mixture was subsequently held for three hours at 400 °C under a nitrogen flow (linear velocity = 20 cm/minute), and the temperature was thereafter raised to 730 °C at a temperature rise rate of 200 °C/hour, and then held for three hours at 730 °C. The entire product obtained by high heat treatment melted and adhered to the interior surface of the reactor, and the height raised to 10 to 18 mm due to bubbling.

(3) Distilled water was put into the reactor, and the treatment product was formed into slurry and removed from the reactor.

(4) The slurry was filtered to collect the solid content, sequentially washed first with 0.1N hydrochloric acid and then with water, filtered, and dried to obtain an

activated carbon with an average particle diameter 20 μm
as the activated carbon of comparative example 11.

Comparative Example 12

Other than setting the ratio of weights [W_2/W_1] of the
5   KOH powder and the carbonaceous material to 6.1/3 = 2.03
using 6.1 g (W_2) of 95%-pure KOH powder having an average
particle diameter of 20 μm, an activated carbon having an
average particle diameter of 20 μm was obtained as the
activated carbon of Comparative Example 12 by the same
10 method as Comparative Example 11, that is, the method that
includes bubbling and the formation of a slurry in the
same manner as described above.

Comparative Example 13

Other than setting the pressure P applied during the
15 molding in tablet form to 1.5 MPa, a tablet product was
molded in the same manner as Example 27 with the same
method as Example 26, and the molded tablet product was
subsequently placed in a reactor that was made from pure
nickel to obtain the activated carbon with an average
20 particle diameter 20 μm of Comparative Example 13 by
performing the processes of steps (2) to (4) in
Comparative Example 11.

Comparative Example 14

Other than setting the pressure P applied during the
25 molding in tablet form to 40 MPa, a tablet product was
molded in the same manner as Example 26 with the same

method as Example 27, and the molded tablet product was subsequently placed in a reactor that was made from pure nickel to obtain the activated carbon with an average particle diameter 20 μm of Comparative Example 14 by

5 performing the processes of steps (2) to (4) in Comparative Example 11.

Comparative Example 15

Other than setting the pressure P applied during the molding in tablet form to 40 MPa, a tablet product was

10 molded in the same manner as Example 26 with the same method as Example 27, and the molded tablet product was subsequently placed in a reactor that was made from pure nickel to obtain an activated carbon with an average particle diameter 20 μm as the activated carbon of

15 Comparative Example 15 by performing the processes of steps (2) to (4) in Comparative Example 11.

(Measurement of the specific surface area and nickel content of activated carbon)

(a) Measurement of the specific surface area

20 Vacuum deaeration treatment was performed for about six hours at 30°C for each of the activated carbons of Examples 26 to 28 and Comparative Examples 11 to 15, 0.1 g samples were subsequently collected from the treatment products, and the specific surface areas of the samples

25 were measured with the aid of an ASSP2010 apparatus manufactured by Shimadzu Corp., in accordance with the BET

method by using version 2.0 of an analysis software program to analyze the distribution of pores. The obtained results are shown in Table 9.

(b) Measurement of nickel content

5   A 0.5 g sample of each activated carbon of Examples 26 to 28 and Comparative Examples 11 to 15 was collected, and the nickel contents of the samples were measured by the wet decomposition method with the aid of an ICP mass analyzer. The results obtained are shown in Table 9.

10   (Manufacture of button-type electric double-layer capacitor)

The activated carbon of Examples 26 to 28 and comparative examples 11 to 15, graphite powder (conductive filler), and PTFE (binder) were weighed so as to achieve a

15 weight ratio of 90:5:5, the weighed products were subsequently kneaded, and an electrode sheet having a thickness of 185 μm was thereafter manufactured by calendering with the aid of a kneader. Two polarizable electrodes having a diameter of 2 mm were cut from the

20 electrode sheet, and the button-type electric double-layer capacitor like Fig. 1 was manufactured as the electric double-layer capacitor of Examples 26 to 28 and Comparative Examples 11 to 15 by using these two polarizable electrodes, a spacer made from PTFE having a

25 diameter of 20 mm and a thickness of 75 μm, an electrolyte, and other components. A propylene carbonate

solution of triethylmethylammonium tetrafluoroborate
$[(C_2H_5)_3CH_3NBF_4]$ (1.8 M) was used as the electrolyte.

(Measurement of the electrostatic capacity of activated carbon)

5   Charge-discharge tests were performed by charging the capacitors for 120 minutes and discharging them for 20 minutes at a charge end-point electric potential of 2.7 V, a discharge end-point electric potential of 0 V, and a charging and discharging current of 5 mA; and the

10   electrostatic capacities (F/cc) of the electric double-layer capacitors of Examples 27 to 29 and Comparative Examples 11 to 15 were calculated with the energy conversion method. The results obtained are shown in Table 9. Additionally shown in the table are the weight

15   ratios $[W_2/W_1]$ of the KOH and carbonaceous material in the mixtures of raw materials for the activated carbon, the types of mixtures, the pressures (MPa) applied when forming the molded product, the nickel contents (ppm) of the activated carbon, and the specific surface areas

20   (m^2/g).

25

Table 9

Activated carbon	W_2/W_1	Type of mixture	Pressure (MPa)	Electro-static capacity (F/cc)	Ni Content (ppm)	Specific surface area (m²/g)
Example 26	1.9	Molded Product	20	33.2	0.2	807
Example 27	1.9	Molded Product	5	33.4	0.1	801
Example 28	1.9	Molded Product	2	32.9	0.1	817
Comparative Example 11	1.9	Powder	–	30.6	30	590
Comparative Example 12	2.03	Powder	–	32.1	47	790
Comparative Example 13	1.9	Molded Product	1.5	32.5	21	795
Comparative Example 14	1.9	Molded Product	40	29	0.4	Not measurable
Comparative Example 15	1.9	Molded Product	40	20.4	0.4	Not measurable

It is apparent from Table 9 that an activated carbon

5   having high electrostatic capacity and minimal nickel

content can be obtained (Examples 26 to 28) when using a

molded product formed under a predetermined pressure. In

this case, it is apparent that the specific surface area

can be controlled to a substantially fixed value by adding

10 conditions such as setting the ratio of both weights

$[W_2/W_1]$ to equivalent values.

In Comparative Examples 11 to 13, it is apparent that

the nickel content is extremely high in comparison with

Examples 26 and 28 due to melting of the powder mixture to

15 adhering to the interior surface of the reactor made from

pure nickel. In the case of Comparative Examples 14 and
15, so the specific surface areas could not be measured
because activation did not sufficiently progress due to
the high density caused by the high pressure and so on.

5

INDUSTRIAL APPLICABILITY

According to the first present invention, a method
for manufacturing activated carbon in which carbonaceous
material is subjected to alkali treatment and activated
10   while kept in a solid state is provided. According to
this manufacturing method, both the carbonaceous material
and the alkali metal hydroxide can be handled in a solid
state, so the method is extremely safe, and corrosion of
an apparatus that occurs when manufacturing an alkali-
15   activated carbon can be greatly reduced. Also, the metal
content of the obtained activated carbon is minimal, so
the electrostatic capacity is large and the chance of
shorting can be reduced when the material is molded and
fabricated into a polarizable electrode, and used in an
20   electric double-layer capacitor.

In the first present invention, by satisfying a
predetermined relationship between the pressure inside the
treatment system and the temperature rise rate during
dehydration treatment when activating carbonaceous
25   material with an alkali to manufacture activated carbon,
the mixture of carbonaceous material and alkali metal

hydroxide can be subjected to dehydration treatment while
kept in the solid state, and corrosion of a device due to
the alkali can be greatly reduced. The carbonaceous
material obtained from the dehydration treatment can be
5   subjected to activation treatment to produce activated
carbon, and can be advantageously used in catalysts,
solvent recovery, water treatment, and as electric double-
layer capacitors or other electrical materials, or the
like.

10   In the first present invention, when inert gas
circulated through the system in at least the activation
step is brought into contact for 0.5 seconds or more with
carbon material for sorption that has been heated to a
temperature of 300 to 800 °C, the alkali metal in vapor
15   form that is generated when an activated carbonaceous
material is activated with an alkali to manufacture
activated carbon can be sorbed to the carbon material for
sorption, making it possible to obtain activated carbon
that is commercially advantageous and can be safely
20   treated while avoiding the danger of ignition and
explosions.

     According to the second present invention, it is
possible to manufacture activated carbon with an
appropriate specific surface area as an electrode for an
25   electric double-layer capacitor with a higher
electrostatic capacity, in which the activation efficiency

can also be improved by means of an alkali metal activator, the consumption thereof can be reduced, the specific surface area can be controlled, thereby resulting in a smaller quantity of impurities.